STUDIES IN THE FIELD OF METAL β-KETOENOLATE CHEMISTRY

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by

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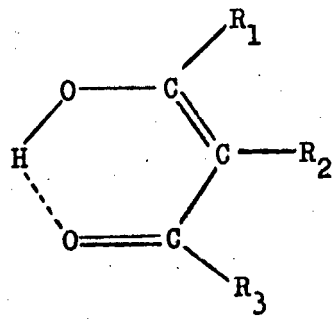
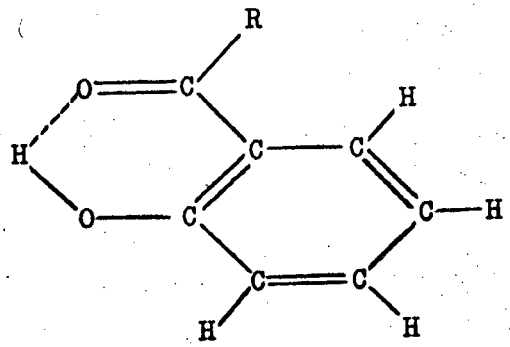
A B B R E V I A T I O N S

abr.	abbreviation.
asym.	asymmetric.
B	any group or adducted molecule.
β-PhEt	β-phenylethyl.
BM	Bohr magneton.
b.p.	boiling point.
Bu	butyl.
Bz	benzyl.
c.f.s.e.	crystal field stabilization energy.
Cx	cyclohexyl.
d.	decomposes.
def.	deformation.
δ	IR bending mode.
en	ethylenediamine.
Et	ethyl.
HL	generalized ligand which coordinates via loss of a proton (e.g. acetylacetone).
i.p.	in plane.
IR	infrared.
L	generalized ligand radical or generalized neutral ligand (e.g. ammonia).
M	central cation in inorganic complex.
Me	methyl.
m.p.	melting point.
NMR	nuclear magnetic resonance.
ν	IR stretching mode.
o.o.p.	out of plane.
Ph	phenyl.
p.p.m.	parts per million.
Pr	propyl.
py	pyridine.
pyNO	pyridine N-oxide.
R	any alkyl or aryl group or any substituent.
s.	sublimes.
sym.	symmetric.
TMS	tetramethylsilane.
UV	ultraviolet.



R_1	R_2	R_3	LIGAND	ABR.
CH_3	H	CH_3	Acetylacetone	ACA
C_6H_5	H	CH_3	Benzoylacetone	BZA
C_6H_5	H	C_6H_5	Dibenzoylmethane	DBM
$t\text{-}C_4H_9$	H	$t\text{-}C_4H_9$	Dipivaloylmethane	DPM
CF_3	H	CH_3	Trifluoroacetylacetone	TFA
CF_3	H	CF_3	Hexafluoroacetylacetone	HFA
$t\text{-}C_4H_9$	H	CH_3	Pivaloylacetone	PVA
OC_2H_5	H	CH_3	Ethylacetoacetate	EAA
CH_3	CH_3	CH_3	3-Methylacetylacetone	MAC
$t\text{-}C_4H_9$	H	CF_3	Pivaloyltrifluoroacetone	PTA
$p\text{-}CH_3OC_6H_5$	H	$p\text{-}CH_3OC_6H_5$	*p,p'*-Dimethoxydibenzoylmethane	p-MeODBM

Formulae and abbreviations of β-diketones studied in this work.



R	LIGAND	ABR.
C_2H_5	*o*-Hydroxypropiophenone	HPP
H	Salicylaldehyde	SAL
OC_2H_5	Ethyl salicylate	ESAL
OCH_3	Methyl salicylate	MSAL
OC_6H_5	Benzyl salicylate	BSAL

Formulae and abbreviations of *o*-hydroxyarylcarbonyl compounds studied in this work.

A B S T R A C T

The syntheses of 188 metal complexes and 19 ligands (the majority of which are newly reported here) are described. These were individually studied by several physical techniques including IR spectroscopy, NMR spectrometry, conductance determinations and magnetic susceptibility determinations. The NMR spectra of 42 variously substituted pyridines were determined.

The results are used to discuss the nature of the bonding and structure of these molecules.

I. INTRODUCTION

1. THE HAMMETT EQUATION

The substituent constant, σ, is a measure of the sum of the inductive (or field) and mesomeric (or resonance) effects of substituents in aromatic molecules. It was found by HAMMETT[1] that linear relationships applied to the rate and the equilibrium constants of practically all side-chain reactions of benzene derivatives. If the logarithms of the rate constants for the hydrolysis of *meta*- and *para*-substituted benzoic esters are plotted against the logarithms of the ionization constants of similarly substituted benzoic acids, a linear relationship results. The straight line graph follows an equation of the form

$$\log k = \rho \log K + C \qquad (1)$$

where k = rate constant of the hydrolysis,

K = ionization constant,

ρ = slope, C = intercept.

Similar linear relationships were found to apply to the rate and equilibrium constants of practically all side-chain reactions of benzene derivatives. It was therefore possible to relate the various series to one standard reference, for which the ionization constants of substituted benzoic acids were especially suitable, because of the many precise values then available.[2] Equation (1) may be simplified to the form

$$\log k = \rho (\log K - \log K^0) + (\rho \log K^0 + C) \qquad (2)$$

where k = any rate or equilibrium constant,

K^0 = the ionization constant of the unsubstituted acid (benzoic acid itself).

The quantity ($\rho \log K^0 + C$) is necessarily equal to $\log k^0$, where k^0 is the rate or equilibrium constant for the hydrolysis of the unsubstituted benzoic ester. Therefore, from equation (2)

$$\log k - \log k^0 = \rho (\log K - \log K^0) \qquad (3)$$

This equation relates to any rate or equilibrium process, but it is convenient to relate all other reaction series to the dissociation of benzoic acids. The substituent constant, σ, is defined as

$$\sigma = \log K - \log K^0 \qquad (4)$$

Thus equation (3) becomes

$$\log k - \log k^0 = \rho\sigma \qquad (5)$$

Equation (5) is more frequently written as

$$\log \frac{k}{k^0} = \rho\sigma \qquad (6)$$

Equation (6) is commonly referred to as the HAMMETT equation.

The substituent constant, σ, is by definition determined by the nature of the substituent, and is normally independent of the nature of the reaction, the constant k of which is involved in equation (5).

Conversely, the reaction constant, ρ, is by the nature of the linear relationship a constant for all substituents, and depends only on the reaction series. It can therefore be seen that the validity of the HAMMETT equation depends on the fact that σ is an expression of the electronic effect of substituents, hence ρ must depend on the effectiveness with which the side chain can transmit the electronic effect of the substituent to the reaction site. The substituent constant σ, is a measure of the electron releasing or electron withdrawing capacity of

a substituent, relative to hydrogen. Electron releasing groups have negative σ values, and electron withdrawing groups have positive σ values. Only *meta* and *para* substituents have been used in the determination of substituent parameters. *Ortho* substituents do not have reliable substituent constants due to steric interference to the reaction imposed by the *ortho* groups. In spite of several attempts to provide a good theoretical foundation or derivation of the HAMMETT equation,[3-4] it has remained fundamentally an empirical relationship.

In all the reaction series studied by HAMMETT, it was found that in one case only, that of the *para*-nitro substituent, it was impossible to represent all reactions with one value of σ. Even in this case, it was not a case of a range of values, but of two widely different ones. One of these values gave satisfactory agreement with the reactions of aniline or phenol derivatives, the other applied to the reactions of all other compounds. The σ values used in this work are not those originally proposed by HAMMETT, but those calculated by JAFFE.[5] In his excellent review on the HAMMETT equation,[5] JAFFE has recalculated all HAMMETT'S original σ values on the basis of the latest values of the ionization and rate or equilibrium constants available from the literature. He also found several other groups which should be given two σ values, one for the reactions of phenol or aniline derivatives, and one for the reactions of all other compounds.

Although the majority of reaction series follow the relationship

$$\log \frac{k}{k^0} = \rho\sigma$$

sometimes certain substituents lie well off the plot of log k/k^0 *vs* σ. In these cases, effective substituent constants, $\bar{\sigma}$, for that particular reaction series may be calculated by drawing the best straight line through the points for normally behaving substituents, determining the slope and calculating $\bar{\sigma}$ from the above equation.

Substituent effects involving substitution of the benzene nucleus have been found to be similar to the situation existing in pyridine systems,[6] in which the nitrogen atom acts as the functional centre. It was suggested that because the reaction centre is within the aromatic nucleus, pyridine reactivities should be particularly sensitive to the effect of substituents. The acid dissociation constants of a wide range of substituted pyridines were determined,[6] and plotted against the HAMMETT σ function. The best straight line was drawn through the points, and effective substituent constants, $\bar{\sigma}$, were calculated as above. The value of ρ was found to be large and positive, this being attributed to the fact that the reaction centre is in the ring. The $\bar{\sigma}$ functions calculated by this method can be used for pyridine systems only. Although in most cases $\sigma - \bar{\sigma}$ was small, indicating the similarity between benzene and pyridine substitution, some values of $\bar{\sigma}$ showed considerable deviation from the same σ values.

The substituent constants σ and $\bar{\sigma}$ discussed above represent a combination of inductive and mesomeric effects. They cannot, therefore, be used for aliphatic molecules. INGOLD[7] has proposed a method for measuring purely polar (inductive) effects in aliphatic molecules by comparing the

relative rates of hydrolysis in acidic and alkaline media of aliphatic esters, where mesomeric effects are eliminated. Following along the lines of INGOLD'S proposal, TAFT[8] gave the following equation for evaluating the polar effects of substituents R in the rates of normal hydrolysis of esters, RCOOR' .

$$\sigma^* = \frac{1}{2.48}\left[\log\,(k/k^0)_B - \log\,(k/k^0)_A\right]$$

k_A and k_B are respective rate constants for the acid and base hydrolysis of the substituted ester, and $k^0{}_A$ and $k^0{}_B$ are respective rate constants for the acid and base hydrolysis of the unsubstituted ester. The factor 2.48 is a constant introduced in an attempt to put the polar effects obtained on about the same scale as the HAMMETT σ values. σ* is a substituent constant dependent only upon the net polar effect of the substituent (corresponding to the rate constant k) relative to that for the standard of comparison (k^0, R = CH_3).

2. SPECTROSCOPIC APPLICATIONS OF THE HAMMETT EQUATION TO ORGANIC SYSTEMS

Infrared spectroscopy has been extensively applied to substituted aromatic, heterocyclic and aliphatic compounds, and correlations between the substituent constant and various IR-active bands have been found to exist. KRUEGER and THOMPSON[9] studied the IR spectra of a number of substituted anilines, finding that a plot of both the symmetric and the asymmetric N-H vibrational frequencies against σ values of the anilines showed on almost linear relationship. KRUEGER and SMITH[10]

studied the IR spectra of a series of primary aliphatic amines, and found that plots of the N-H stretching frequencies against σ* gave trends similar to those found for aromatic amines. For both aliphatic and aromatic amines it was observed that as the substituent becomes more electron withdrawing, the N-H frequencies increase, *i.e.* the N-H bond is strengthened. KRUEGER and SMITH explain these trends by suggesting that as the electron donating power of the substituent increases, the apparent electronegativity of the nitrogen atom decreases because of increased electron density, consequently binding the hydrogen atoms less firmly, resulting in a lowering of the bond strengths and hence stretching frequencies.

The C=O stretching frequency of a series of aliphatic ketones of the type RR'C=O has been examined by THOMPSON and JAMESON[11]. They have found that a plot of the frequency of absorption in the IR spectrum of the carbonyl group against the sum of σ* for R and R' exhibits a linear relationship, electron withdrawal resulting in a strengthening of the C=O bond. The authors do not attempt to explain this result but the strengthening of the C=O bond is probably due to electron withdrawal reducing the normal inductive effect of the carbonyl group.

STONE and THOMPSON[12] have studied the O-H stretching frequencies of a number of substituted aromatic phenols, and have observed a linear relationship of the position of the IR frequency of the O-H vibration against the HAMMETT σ function, indicating a weakening of the O-H bond with increasing electron withdrawal, as would be expected.

LILER[13] has observed a linear correlation between the carbonyl frequency in compounds RCOX (where R is an aliphatic or aromatic radical) and HAMMETT'S *meta* σ constants of the group X, which is directly bound to the carbon atom. It has been suggested by TAFT[14] that since HAMMETT'S *meta* σ values measure the effect of the substituent in a benzene ring on the electron density on the carbon atom in the *meta* position, any change in electron density at this position affects the reaction centre further purely inductively, since no direct conjugation between the reaction centre and the *meta* substituent in the benzene ring is possible. The *meta* σ values may, therefore, be regarded as measuring the inductive effect of the substituent, thus explaining the relationship obtained by LILER. Electron withdrawal was found to strengthen the C=O bond, as was found by THOMPSON and JAMESON[11].

No IR studies of the above nature have been performed on a series of substituted pyridines, probably due to the fact that there is no IR absorption which can be unambiguously assigned as being due to one specific vibration of the pyridine nucleus. Most absorptions in the IR due to the pyridine nucleus are coupled due to extensive electron delocalization. Consequently, substituent effects will affect the ring as a whole, thus giving shifts of very small magnitude.

Nuclear magnetic spectrometry has also been used to show correlations between the substituent function and NMR signals of various protons in similarly substituted organic molecules.

PATERSON and TIPMAN[15] studied the NMR spectra of a series of *para*- substituted phenols. Whilst no correlation between the phenolic proton and the HAMMETT σ function was apparent, an approximately linear relationship was demonstrated between the ring protons and the HAMMETT *para* σ function (σ_p). It was found that electron releasing substituents caused deshielding of the ring protons. Although this was not explained by the authors, this effect could be due to the decreased possibility of the formation of the quinonoid resonance form on electron release into the ring.

In a study of the NMR spectra of variously substituted anilines, DYAL[16] has reported that a linear relationship was observed between the chemical shifts of the amino protons and the substituent constant. It was found that electron withdrawal by the substituent caused deshielding of the amino protons, as would be expected. These results were found to hold for three different solvents, acetonitrile, carbon tetrachloride and deuterochloroform.

An NMR study by KONDO and colleagues[17] showed a linear relationship between the chemical shifts of the carboxylic proton of monosubstituted benzoic acids at infinite dilution in pyridine, and the HAMMETT σ values. It was demonstrated that electron withdrawal caused deshielding of the carboxylic proton, as would be expected.

A number of NMR studies have been reported[14, 18-20] on the effect of substituents on the magnetic shielding of a proton bound directly to a benzene ring. It has been shown that, although

the chemical shifts of the proton *para* to the substituent show a trend towards correlation with the HAMMETT σ values, no such correlation exists for the *meta* proton shifts. It was shown (for monosubstituted benzene derivatives) that the *para* proton was deshielded by electron withdrawal of the substituent, as would be expected.

Many NMR studies have been reported[21-24] concerning pyridine and substituted pyridines, however most were concerned only with assignment of the signals, both by empirical means and deuterium substitution of the various protons. One of these studies[21] deals with the application of the HAMMETT σ function to a series of 2-substituted pyridines. It was found that an approximate linear relationship existed between the σ value of the 2-substituent and the chemical shift of the proton *para* to the substituent, *i.e.* the proton in the 5-position. It was found that electron withdrawal by the substituent caused deshielding of the *para*- proton, as would be expected.

It is of interest to note that correlations have been found[25-26] between IR frequencies and signals in the NMR spectra of the same compounds. Thus it has been found[25] that a plot of the C=O stretching frequency against the chemical shift of the hydroxylic proton in a series of β-diketones produces a linear relationship, the carbonyl stretching frequency decreasing with increased deshielding of the hydroxylic proton. It has been demonstrated by other workers[26] that plots of the chemical shift of the hydroxylic proton against the IR absorption of the same proton in the same type of compounds also gave rise to a

linear relationship, the strength of the O-H bond decreasing with increased deshielding of the same proton.

3. APPLICATIONS OF THE HAMMETT EQUATION TO METAL COMPLEXES; THE STABILIZATION FACTOR

There have, therefore, been many studies of substituted organic compounds, and correlations have been found between substituent constants and group frequencies or chemical shifts, but there have been few similar studies applied to a series of coordination compounds containing organic ligands, individual members of which differ only in the substituent on the ligand. Although metal complexes of substituted pyridines have been studied for many years, only one systematic study[27] has attempted to estimate the coordination bond strength as affected by the substituent on the pyridine ring. In that investigation, the relative Ag-N bond strengths of silver complexes of substituted pyridines were studied by comparing their stability constants in aqueous solution. The absence of a linear relationship between these stability constants and the basicity of the free ligands was attributed to back-donation of electrons from the metal to the metal-ligand bond (metal-ligand π-bonding). PAULING[28] has also explained the stability of certain complexes on the basis of metal-ligand double bonding. He suggested that the transition elements can use, for multiple bonding, lower energy d-orbital electrons which are either not available or of unsuitable energy in the non-transition elements. Although there is no direct proof of metal-ligand π-bonding in aliphatic and aromatic amine complexes and although such π-bonding would not be anticipated

on theoretical grounds, several experimental observations have been rationalized on this basis.

Recently IRVING, DA SILVA and CALADO[29-30] analysed the stability constant data from several studies on metal complexes of substituted organic ligands and derived a stabilization factor, S_f, which is related to the additional stabilization caused by the formation of a metal-ligand π-bond. S_f is a parameter derived on thermodynamic grounds as follows. Consider the free energy change accompanying a reaction subject to the variable x_1, x_2, x_3, ----

$$d\Delta G^0 = \sum_i \left(\frac{\delta \Delta G^0}{\delta x_i} \right) dx_i \qquad (1)$$

Suppose all the variables are constant, except one (*e.g.* the charge density at the reaction centre arising from the nature of the substituent, x_i). Then

$$d\Delta G^0 = \left(\frac{\delta \Delta G^0}{\delta x} \right) dx \qquad (2)$$

Assuming that the partial derivative is constant in the range of variation of x, equation (2) can be integrated.

$$\Delta G^0_i - \Delta G^0_o = \left(\frac{\delta \Delta G^0}{\delta x} \right) (x_i - x_o) \qquad (3)$$

where $\Delta G^0 = -RT\ell nK$

Consider two different reaction series A and B, each similarly affected by the variable x. Then

$$RT\ell n \frac{K_i^A}{K_o^A} = \left(\frac{\delta \Delta G^0}{\delta x}\right)^A (x_o - x_i)^A \qquad (4)$$

and

$$RT\ell n \frac{K_i^B}{K_o^B} = \left(\frac{\delta \Delta G^0}{\delta x}\right)^B (x_o - x_i)^B \qquad (5)$$

Let $g_x = \left(\frac{\delta \Delta G^0}{\delta x}\right)$

then

$$\log \frac{K_i^B}{K_o^B} = \frac{g_x^B}{g_x^A} \cdot \frac{(x_i - x_o)^B}{(x_i - x_o)^A} \log \frac{K_i^A}{K_o^A} \qquad (6)$$

where $\frac{(x_i - x_o)^B}{(x_i - x_o)^A}$ is a constant characteristic of the reaction series A and B, and is approximately equal to 1 if the effect of the substituent on reactions A and B is not very different and $\frac{g_x^B}{g_x^A}$ describes the relative effects on the free energy change accompanying the process of the variable x. Generally this is not equal to 1 but is a constant characteristic of the reactions A and B. Let this value be equal to J_x^{AB}, then

$$\log \frac{K_i^B}{K_o^B} = J_x^{AB} \log \frac{K_i^A}{K_o^A} \qquad (7)$$

These results can now be applied to a series of reactions A, corresponding to the acid dissociation of several ligands HnL, HnL', *etc.*

$$HnL \rightleftarrows L + nH,$$

$$HnL' \rightleftarrows L' + nH, \text{ etc.},$$

and B, corresponding to the complexation of a metal ion M by

the same ligands

$$HnL + M \rightleftarrows ML + nH,$$

$$HnL' + M \rightleftarrows ML' + nH, \text{ etc.}$$

The equilibrium constant for reaction A is given by

$$K_{HnL} = \frac{[H]^n[L]}{[HnL]}$$

The equilibrium constant for reaction B is given by

$$K_L = \frac{[ML][H]n}{[HnL][M]}$$

$$= \frac{[ML]}{[M][L]} \cdot \frac{[H]^n[L]}{[HnL]}$$

$$= \beta_{ML} \cdot \frac{1}{\beta_{HL}}$$

where β_{ML} = the stability constant of the complex

and β_{HL} = the association constant of the ligand.

Therefore $K_L = \frac{\beta_{ML}}{\beta_{HL}}$

Substituting in equation (7)

$$\log \frac{K_{L'}}{K_L} = J_x^{AB} \log \frac{K_{HL}}{K_{HL'}} \qquad (8)$$

therefore

$$\log \frac{\beta_{ML'}/\beta_{HL'}}{\beta_{ML}/\beta_{HL}} = J_x^{AB} \log \frac{K_{HL}}{K_{HL'}} \qquad (9)$$

showing the relative influence of a substituent group in the dissociation constants of the ligands and the corresponding stability of the complexes. The left-hand side of equation (9) is the stabilization factor, S_f. This factor was shown

to be a measure of the π-stabilization additional to σ-bond formation by back donation of d-electrons from the metal to antibonding orbitals in the ligand. Therefore

$$S_f = J_x^{AB} \log \frac{K_{HL'}}{K_{HL}} \qquad (10)$$

$\log \frac{K_{HL'}}{K_{HL}}$ can be identified with the product ρσ of the HAMMETT equation. It would be equal to σ if the values of K referred to benzoic acids (ρ = 1 for benzoic acids). Equation (10) can therefore take the simpler form

$$S_f = J_x^{AB} \rho\sigma \qquad (11)$$

Therefore

$$S_f = \rho'\sigma \qquad (12)$$

showing a direct proportionality between the stabilization factor, S_f, and the HAMMETT σ function.

DA SILVA and CALADO[30] used the above equations to calculate S_f values for several series of metal complexes, including silver(I) complexes of substituted pyridines and substituted anilines, copper(II) complexes of substituted benzoic acids and substituted pyridine adducts of copper(II) acetylacetonate. Dissociation constants of the ligands and stability constants of the metal complexes were obtained from previously published work. For the anilines and benzoic acids, the σ values of JAFFE[5] were used. For the pyridines, the $\bar{\sigma}$ values of FISCHER[6] *et. al.* were used. It was found in all cases that plots of the calculated S_f values for the complexes against the σ or $\bar{\sigma}$ values resulted in excellent linear relationships, the slopes indicating additional stabilization of the

4. METAL β-KETOENOLATES AND THEIR BASE ADDUCTS

β-Diketones are known to form stable six-membered chelates with many elements. The acetylacetonates are the best known examples of these complexes. Acetylacetone reacts with the metal through the enol form, satisfying the primary valence of the metal ion by an enolic hydroxide residue and the secondary valence by the oxygen atom of the carbonyl group. Dioxobis(acetylacetonato)uranium(VI) and its solvates have been extensively studied. The preparation of the hydrated complex[34], the anhydrous complex,[35-37] the pyridine adduct[38] and various other solvates[39] have been reported. The preparations of various uranyl β-ketoenolates have been reported.[40-43] IR studies,[39,44] UV studies,[39,45] magnetic susceptibility studies,[39] electrical conductivity studies,[39] thermogravimetric analyses,[46] differential thermal analyses[46] and heats of solvation studies[46-47] have all been recorded for variously solvated forms of uranyl β-ketoenolates. An X-ray crystallographic study[48] has been performed on hydrated $UO_2(ACA)_2$. Most uranyl β-ketoenolate complexes are remarkably stable. The most significant feature of the IR spectra of these compounds is a very intense band in the region of 900 cm^{-1} which has been assigned[39] to the U=O asymmetric stretching frequency, and a strong peak in the region of 270 cm^{-1} which has been assigned[49] to the O=U=O bending mode of the uranyl group. Many X-ray crystallographic studies[48,50-54] performed on various uranyl compounds indicate that the O=U=O group is linear. This is confirmed by the IR evidence[39,44] since no U=O symmetric stretching frequency is observed, however,

Raman evidence[55] appears to favour non-linearity of the O=U=O group in ionic uranyl compounds.

Vanadyl acetylacetonate was first prepared by MORGAN and MOSS[56] by mixing solutions of vanadyl sulphate and acetylacetone, and neutralizing the mixture. The product thus formed was formulated $VO(ACA)_2$, although later workers[57] formulated the product as the monohydrate, $VO(ACA)_2 \cdot H_2O$. It has been found[58] that the product formed under completely anhydrous conditions is identical to that described above, also no absorptions in the IR due to coordinated water are apparent, hence the former formulation is taken as being correct. More recently, an X-ray crystallographic study[59] has shown the compound to be anhydrous, being square pyramidal in structure, the vanadium atom being placed above the base of the pyramid approximately at its centre of gravity. Molecular weight determinations[58] indicate that the compound is monomeric in benzene. $VO(ACA)_2$ forms base adducts with pyridines and piperidines,[58] while adducts of primary aliphatic amines are not very stable and attempts to prepare primary aromatic amine adducts in these laboratories have met with no success. Pyridine N-oxides have been shown[60] to form adducts with $VO(ACA)_2$. Substituted pyridines form adducts with $VO(ACA)_2$[61] but it would appear that the reaction products are a mixture of geometric isomers. Many different β-ketoenolate complexes of the vanadyl moiety have been prepared.[60,62-63] The most significant feature of the IR spectra of these compounds is an intense band in the 930 to 1000 cm^{-1} region which has been assigned to the V=O stretching frequency.[64-65]

The IR stretching vibrations of these two bonds are therefore expected to be close together in the IR spectrum. In fact, two bands are observed in the 1500-1625 cm^{-1} region, where these two absorptions would be expected. Some confusion exists in the literature with reference to the assignment of these two bands. The first attempts to distinguish between the C=O and C=C stretching vibrations were made by LECOMPTE.[75-76] By considering acetylacetone to be a combination of two molecules of acetone, he empirically assigned the higher band to the C=O stretch and the lower band to the C=C stretch. BELLAMY and BRANCH[77] also considered the problem and suggested that, since the C=O stretch in organic molecules is usually more intense than the C=C stretch, the more intense of the two bands should be assigned as the C=O stretch, regardless of position.

NAKAMOTO *et.al.*,[78] on the basis of a normal coordinate treatment of copper(II) acetylacetonate, assigned the higher band to the C=C stretch, and the lower band to the C=O stretch. The problem was somewhat simplified, however, by considering a single ring only, and neglecting interactions between the two chelate rings. A further simplification was made in assuming the methyl group to be a single atom of mass 15 a.m.u. Further work by NAKAMOTO *et.al.*[79-80] indicated that these assignments were correct. SHIMANOUCHI *et.al.*[81] undertook a more refined treatment in which the complete 29-body problem (for copper(II) acetylacetonate) and 43-body problem (for iron(III) acetylacetonate) were worked out. The conclusion substantially supported the earlier work of NAKAMOTO, but was practically simultaneously reversed by a further theoretical

treatment by BEHNKE and NAKAMOTO[82] in which the higher frequency band was assigned as the C=O stretch (νC=O) and the lower as the C=C stretch (νC=C). A recent IR spectral study[83] of the ^{18}O-labelled acetylacetone chelates of chromium(III) and manganese(III) has confirmed these assignments. When the IR spectra of the normal acetylacetonates were compared with those of the isotopically labelled complexes, it was found that a reduction of 13 cm^{-1} occurred with the higher band, whilst no change was observed for the lower band.

In phenyl-substituted β-ketoenolates the 1500-1600 cm^{-1} region of the spectrum is slightly more complex, due to the fact that aromatic C=C stretches are observed in this region. In fact, three bands are observed in this region. NAKAMOTO[79] has performed perturbation calculations for the dibenzoylmethanate complexes of copper(II) and nickel(II), based on the normal coordinate treatment of copper(II) acetylacetonate. He concluded that the band of highest frequency was νC=C, the next band νC=O and the lowest band due to a combination of νC=O and C-H bend (δC-H), with none of the bands in this region being due to phenyl absorption. It has been demonstrated by HANCOCK and THORNTON[84] that νC=O in the IR spectra of a series of trivalent transition metal acetylacetonates is sensitive to change of metal, νC=C exhibiting an inverse relationship to the frequency trend observed for νC=O. In the analogous phenyl-substituted complexes it was demonstrated that the first band is almost insensitive to change of metal, and is therefore assigned to νC=C of the phenyl rings. The second and third bands exhibit the degree of sensitivity to change of metal observed for νC=O and νC=C of the analogous

acetylacetonates and are therefore assigned as νC=O and νC=C respectively. These assignments are supported by the results of a study[85] of the ^{18}O-labelled dibenzoylmethane chelate of copper(II).

The metal to oxygen (M-O) vibrations are of great importance in studies of base adducts of metal β-ketoenolates since metal to pyridine bands occur below the lower limit (200 cm^{-1}) of the IR spectrophotometer used in this study.[86-88] The IR spectra of acetylacetonate complexes show three bands in the region of 650, 550 and 420 cm^{-1}. These have been assigned by NAKAMOTO[78] as: (νM-O + νC-CH_3); (νM-O + ring def.) and νM-O, respectively. PINCHAS and colleagues[83] in their study of ^{18}O-labelled acetylacetonates observed that the band in the 650 cm^{-1} region was only slightly shifted on insertion of the heavier isotope and this band was therefore re-assigned to an out-of-plane deformation mode. The two other bands in the regions 550 and 420 cm^{-1} were both affected by insertion of the heavier isotope, the band in the 550 cm^{-1} region showing greater sensitivity than the band in the 420 cm^{-1} region. The band at 550 cm^{-1} was therefore assigned as being composed of a greater percentage of M-O character than the band at approximately 420 cm^{-1}, whereas NAKAMOTO assigns the latter as pure νM-O.

It seems improbable that any one of the bands in the 400-700 cm^{-1} region of the IR spectrum can be assigned to a pure M-O mode since any IR active mode will probably comprise coupling with ligand modes.

II. EXPERIMENTAL

1. PHYSICAL TECHNIQUES

a. Infrared Spectroscopy

The IR spectra were obtained in the 4000-200cm^{-1} region on a Beckman IR-12 spectrophotometer, calibrated against carbon dioxide and water vapour. During the earlier stages of this work, spectra were recorded on a Beckman IR-8 spectrophotometer, but with full-time availability of a Beckman IR-12, all spectra were re-determined on the latter instrument which has superior resolution and reproducibility.

Originally compounds were sampled as KBr or CsI pellets, but it was later found that the nujol mull technique gave spectra with better definition, so that all compounds were redetermined using the latter technique. KBr or CsBr plates were used to house the mulled samples. An extensive test of the reproducibility of frequencies of metal β-ketoenolates alternatively sampled as nujol mulls, CsBr pellets and chloroform solutions has been made[89] in this laboratory. No material discrepancies were noted. Solution spectra were not determined in the present work.

Because it was necessary in some cases to determine small frequency shifts *e.g.* νM-O of the substituted pyridine adducts of nickel(II) acetylacetonate, the transmission minima of interest were determined by horizontal and vertical scale expansion, which is possible directly on the IR-12. The

frequencies were read directly from the frequency drum and not from the chart paper, thus eliminating any error which may arise from backlash in the gears or from lack of precision in the calibration of the chart paper. The latter was, on occasion, found to be appreciable. Using this method, reproducibility and precision of 1 cm^{-1} was obtained in the 2000-200 cm^{-1} region and of 2 cm^{-1} in the 4000-2000 cm^{-1} region. This error was determined by obtaining several spectra from the same mull, several spectra from different mulls, and finally by repeating the whole process with a sample from a different batch.

The makers of the Beckman IR-12 report a resolution of better than 0.5 cm^{-1} in the 2000-200 cm^{-1} region and better than 1 cm^{-1} in the 4000-2000 cm^{-1} region.

b. Nuclear Magnetic Resonance Spectrometry

The NMR spectra were obtained as approximately 100 mgm/ml $CDCl_3$ solutions, using a Varian A-60 spectrometer. Tetramethylsilane (TMS) was used as internal calibrant. Chemical shifts were measured in p.p.m. downfield from the reference signal. D_2O exchange was carried out by the addition of approximately 0.3 ml of D_2O to the $CDCl_3$ solution, shaking the sample tube vigorously, allowing to settle and then redetermining the spectrum.

c. Magnetic Moment Determinations

Magnetic susceptibilities were determined on a Newport-Stanton single temperature magnetic balance, consisting of a

semi-micro analytical balance, a water-cooled electromagnet and an associated power supply.

If a cylindrical specimen is suspended in a magnetic field with the lower end in the region of maximum field and the upper end in a region of effectively zero field, it can be shown that the gram susceptibility of the specimen is given by

$$\chi = \frac{(\kappa v + Bw)}{W} \qquad (1)$$

where κ is the volume susceptibility of air = $0{\cdot}029 \times 10^{-6}$ (in c.g.s. units); v is the volume of the specimen; w is the force exerted on the specimen; B is the tube constant involving the dimensions of the specimen and the field strength, and is determined by calibration of the tube with mercury tetrathiocyanatocobalt(III) for which the gram susceptibility is precisely known, *viz.* $16{\cdot}44 \times 10^{-6}$ (in c.g.s. units); W is the weight of the specimen.

v is obtained from [(weight of tube filled with water)-(weight of empty tube)] /density of water at t^0C. W is obtained from [(weight of tube filled with specimen)-(weight of empty tube)] in grams. w is obtained from [(weight of tube with specimen, magnet "on")-(weight of tube with specimen, magnet "off")-(diamagnetic force of tube)] in milligrams. χ can now be calculated from equation (1).

The molar magnetic susceptibility (χ_M) is the product of the gram susceptibility and the molecular weight of the complex.

Allowance must be made for the diamagnetism of the ligands, which can be calculated.[90-91] The correction is applied to determine the susceptibility of the metal ion, χ_A, by

$$\chi_A = \chi_M + \chi_L$$

where χ_L is the total susceptibility of the ligands.

The magnetic moment, μ, may be calculated from

$$\mu = 2.84(\chi_A T)^{\frac{1}{2}}$$

where T is the absolute temperature.

The number of unpaired electrons of the metal ion may be calculated from the "spin only" formula

$$\mu = \left[n(n+2)\right]^{\frac{1}{2}}$$

where n is the number of unpaired electrons, and is normally an integer for mononuclear complexes.

The measurements were made in duplicate at four different field strengths, the tube being repacked for each determination.

d. Conductivity Measurements

The conductance measurements were determined on a Metrohm model E 382 conductometer at 25°C in methanol and nitrobenzene with a final concentration of 0.001M. The conductivity cell had a cell constant of 0.69 cm^{-1}. The molar conductances were calculated thus:

The resistance (R) of a conductor is directly proportional to its length (L) and inversely proportional to its area of cross-section (a).

$$R = \rho \frac{L}{a} \quad (1)$$

ρ, the constant of proportionality, is termed the specific resistance. Specific conductance (κ) is the reciprocal.

$$\kappa = \frac{1}{\rho} \quad (2)$$

$$\text{Therefore } \kappa = \frac{L}{aR} \quad (3)$$

$$\text{The cell constant } k = \frac{L}{a} \quad (4)$$

$$\text{Thus } \kappa = \frac{k}{R} \quad (5)$$

$$\text{Therefore } \kappa = k\bar{C} \quad (6)$$

where $\bar{C}$ is the conductance in ohms $^{-1}$cm^2.

Molar conductance, Y, is given by

$$Y = \frac{1000\kappa}{c} \quad (7)$$

where c = concentration in g equiv litre^{-1}.

To determine the molar conductance for a solution of concentration c g equiv litre^{-1}, the resistance R, is measured and hence κ determined from equation (5), where the cell constant, k, is equal to 0·69 cm^{-1}. Hence the molar conductance can be calculated from equation (7).

e. Melting Points

All melting points quoted herein are corrected, and were determined on a Kofler hot stage.

f. Microanalyses

Microanalyses were performed by Dr. F. Pascher, Bonn, and Dr. K.G. Fuhr, of this Department.

g. Uranium Analyses

Uranium analyses[39] were performed by the author (ignition to 750-850^{0}C for several hours, and weighing the residual U_3O_8).

2. PREPARATION OF COMPOUNDS

In the syntheses of compounds given below the word "mole" should be construed as "molar proportion".

a. Hydrated Uranyl β-Ketoenolates[34,39,41,45]

The hydrated uranyl complexes of HACA, HBZA, HDBM and HTFA were all prepared by a similar method. Uranyl acetate dihydrate (1 gm, 1 mole) was dissolved in water (40 ml) and warmed to 60°. The appropriate ligand (2 mole) was dissolved in methanol (10 ml), warmed to 60° and added to the uranyl solution. The mixture was heated on a water bath (1 hr) and allowed to cool to room temperature. The yellow-orange precipitate was filtered at the pump and air dried. The complex derived from HDBM is exceptional in that mixing of the two solutions causes immediate precipitation of the complex.

The hydrated uranyl complex of HDPM was prepared in a completely different manner. Uranyl acetate dihydrate (1 gm, 1 mole) was dissolved in methanol (10 ml) to which was added HDPM (2 mole) and pyridine (1 mole). The pyridine adduct of uranyl dipivaloylmethanate separates out as orange crystals after allowing the mixture to stand (24 hr). This complex was sublimed under reduced pressure. At approximately 150°, a small amount of the orange complex sublimed, leaving a large mass of deep red crystals in the tube. This is hydrated uranyl dipivaloylmethanate. The HDPM was prepared as reported in the literature[99] by the condensation of t-butyl methyl ketone (pinacolone) with methyl t-butyrate (methyl pivalate).

b. Anhydrous Uranyl β-Ketoenolates [35,40,44-45]

Of the ligands employed in this work, only HACA, HBZA, and HDBM formed anhydrous uranyl complexes. These were obtained by placing the hydrated complex in a drying pistol (105^0/0.5 mm Hg/24 hr). The products are stable and do not readily re-absorb water from the atmosphere, contrary to earlier reports.[35]

c. Pyridine Adducts of Uranyl β-Ketoenolates [38,44-45]

Pyridine adducts of the following uranyl β-ketoenolates were prepared: UO_2L_2 (L = ACA, BZA, DBM, DPM, TFA, PVA, EAA, MAC). The HPVA was prepared by condensation of pinacolone with ethyl acetate.

The pyridine adducts of UO_2L_2 (L = ACA, PVA, TFA, DPM) were prepared by dissolving uranyl acetate (1 gm, 1 mole) in methanol (5 ml) and adding a mixture of β-diketone (2 mole) and pyridine (1 mole). This was allowed to stand (24 hr). The resulting yellow-orange crystals were filtered at the pump and air dried.

The pyridine adduct of $UO_2(DBM)_2$ was prepared by dissolving $UO_2(DBM)_2 \cdot H_2O$ (1 gm, 1 mole) in ether (30 ml) and adding pyridine (1 mole). A crystalline precipitate suddenly formed. This was allowed to stand (1 hr), filtered at the pump and air dried.

The pyridine adduct of $UO_2(BZA)_2$ was prepared by dissolving $UO_2(BZA)_2 \cdot H_2O$ (1 gm, 1 mole) in methanol (30 ml) and adding pyridine (1 mole). The mixture was heated on a steam bath (30 min) when a precipitate started to form. It was removed from the bath and allowed to stand (24 hr). The resultant

complex was filtered at the pump and air dried.

d. Pyridine N-Oxide Adducts of Uranyl β-Ketoenolates

Pyridine N-oxide adducts of the following complexes: UO_2L_2 (L = ACA, DPM, TFA, DBM, BZA) were prepared by the same method used to prepare the pyridine adducts, substituting pyridine N-oxide for pyridine. The products were filtered at the pump, washed successively with methanol and ether, and air dried.

e. Pyridine Adducts of Uranyl *o*-Hydroxyarylcarbonyl Compounds

Pyridine adducts of the following uranyl *o*-hydroxyarylcarbonyl complexes: UO_2L_2 (L = ESAL, MSAL, HPP, BSAL, SAL) were prepared by dissolving uranyl nitrate hexahydrate (1 gm, 1 mole) in methanol (10 ml) and adding a mixture of the *o*-hydroxyarylcarbonyl compound (2 mole) and pyridine (1 mole). The mixture was heated on a water bath (1 hr) and allowed to stand (24 hr). The resulting dark red-orange crystals were filtered at the pump, washed successively with methanol and ether, and air dried.

Many other *o*-hydroxyarylcarbonyl compounds were attempte as ligands, but were unsuccessful. Many attempts were made to prepare the hydrated uranyl *o*-hydroxyarylcarbonyl complexes, but none of the attempts succeeded.

f. Substituted Pyridine Adducts of Uranyl Acetylacetonate

A range of 3- and 4-substituted pyridines was used to synthesize a series of substituted pyridine adducts of uranyl acetylacetonate. A total of twenty-six complexes of this

nature were prepared.

The general method of preparation was to dissolve uranyl acetate dihydrate (1 gm, 1 mole) in methanol (10 to 20 ml). A mixture of acetylacetone (2 mole) and the substituted pyridine (1 mole) was added. The mixture was set aside (24 hr) and the orange-yellow complex filtered at the pump, washed successively with methanol and ether, and air dried.

Variations of the above procedure included substitution of uranyl nitrate hexahydrate for the uranyl acetate dihydrate, heating the final mixture on a water bath for a short time and, in the case of solid substituted pyridines, dissolving the pyridine in methanol before addition to the uranyl solution.

If none of the above variations produced the required complex an alternative method was adopted. This consisted of dissolving anhydrous $UO_2(ACA)_2$ (1 gm, 1 mole) in ether (50 ml), adding the substituted pyridine (1 mole), evaporating the mixture down to 25 ml on a water bath and allowing to stand (12 hr). The complex thus formed was filtered at the pump, washed with ether and air dried.

The latter procedure is to be preferred where yields are of importance.

g. Substituted Pyridine Adducts of Uranyl Dibenzoylmethanate

A series of four variously-substituted pyridine adducts of $UO_2(DBM)_2$ was prepared.

The method of preparation was the same as that of the pyridine adduct of $UO_2(DBM)_2$. In some cases the solution had to be heated on a water bath before the complex would

precipitate. The resulting complexes were washed with ether and air dried.

h. Substituted Pyridine Adducts of Uranyl Benzoylacetonate

A series of four variously-substituted pyridine adducts of $UO_2(BZA)_2$ was synthesized.

The method of preparation is the same as that of the pyridine adduct of $UO_2(BZA)_2$. The resulting complexes were filtered at the pump, washed successively with methanol and ether and air dried.

i. Substituted Pyridine Adducts of Uranyl Dipivaloylmethanate

A series of four variously-substituted pyridine adducts of uranyl dipivaloylmethanate was prepared.

The method of preparation is the same as that of the pyridine adduct of $UO_2(DPM)_2$. The resulting complexes were filtered at the pump, washed successively with methanol and ether and air dried.

j. Substituted Pyridine Complexes of Zinc Chloride [86]

A series of four variously-substituted pyridine complexes of zinc chloride was prepared.

Zinc chloride (1 gm, 1 mole) was dissolved in ethanol (30 ml) to which a solution of the substituted pyridine (1 mole) in ethanol (20 ml) was added. The complex precipitated immediately or after brief shaking. The white complexes were recrystallized from ethanol, filtered at the pump, washed

β-ketoimine collected.

Exceptions to the above method were employed for the β-ketoimines resulting from the reaction of acetylacetone with methylamine, ammonia, t-butylamine and aniline.

The methylimine was prepared by reaction of acetylacetone with a 33%(w/w) solution of methylamine in ethanol. The ethanol distils at a lower temperature than the imine.

The monoimine was synthesized by reaction of acetylacetone with a 25%(v/v) solution of ammonia in water. The water distils at a lower temperature than the imine.

The t-butylimine was prepared by reaction of acetylacetone with t-butylamine. When the two reactants were mixed, a white solid formed, probably the t-butylamine salt of acetylacetone. This was dissolved with a small amount of ethanol and the mixture refluxed (3 hr). The ethanol distils at a temperature lower than that of the imine.

The anilide was synthesized by reaction of acetylacetone with aniline. When the two reactants were mixed, no vigorous reaction ensued and the mixture was refluxed (6 hr) before distilling off the imine.

Some of the imines with high boiling points were distilled under reduced pressure (1.0 mm Hg) to obtain pure samples for analysis.

m. Primary Aliphatic Amine Adducts of Uranyl Dibenzoylmethanate [45]

A series of thirteen primary aliphatic amine adducts of $UO_2(DBM)_2$ was synthesized. $UO_2(DBM)_2 \cdot H_2O$ (1 gm, 1 mole) was dissolved in ether (50 ml) and the primary aliphatic amine (1 mole) was added to the solution and allowed to stand (24 hr).

The resulting complexes were filtered at the pump, washed with ether and air dried.

The only exception to the above method was the preparation of the ammonia adduct. In this case gaseous ammonia was bubbled through an ethereal solution of the uranyl complex and the ammonia adduct was precipitated immediately.

n. Primary Aliphatic Amine Adducts of Uranyl *p,p'*-Dimethoxydibenzoylmethanate.

p,p'-Dimethoxydibenzoylmethane was prepared by a modification of the general method of ADAMS and HAUSER.[94-96]

Sodium (20 gm) was cut into small pieces and weighed under anhydrous ether. This was slowly added, portionwise, to an excess of liquid ammonia containing one small crystal of iron(III) nitrate. The mixture was mechanically stirred while liquid ammonia was continuously added to replace that which had boiled off, and to ensure that all the sodium had reacted to form sodamide. When the reaction was complete anhydrous ether was added, and the mixture was heated with a hot air blower until the excess liquid ammonia had boiled off. This stage is reached when the ether commences to reflux. The suspension of sodamide in ether was then refluxed (10 min) whilst stirring was continued.

p-Methoxyacetophenone (39 gm) in anhydrous ether (50 ml was slowly added over 10 min. The suspension changed colour at this stage, going from grey to yellow. A solution of methyl *p*-methoxybenzoate (43 gm) in anhydrous ether (50 ml) was slowly added over 10 min. The yellow suspension turned brown.

The suspension was refluxed (2 hr) and allowed to stand (18 hr). The mixture was poured into water (300 ml) causing considerable effervescence, probably due to the decomposition of excess sodamide. Hydrochloric acid (5M) was added to neutralize the mixture which was extracted four times with ether (4 x 100 ml). The ether solution was allowed to evaporate to dryness (48 hr) and the residue taken up in ethanol (500 ml), boiled, filtered and allowed to cool. The crystalline mass which separated was filtered at the pump and recrystallized from ethanol to give fine yellow crystals; yield 23 gm (30%).

The hydrated uranyl complex of the above ligand was prepared in an analogous manner to $UO_2(DBM)_2 \cdot H_2O$.

The primary aliphatic amine adducts of $UO_2(p\text{-MeODBM})_2$ were synthesized in an analogous manner to the primary aliphatic amine adducts of $UO_2(DBM)_2$.

o. Anhydrous Vanadyl β-Ketoenolates [56-58,63,97]

The vanadyl complexes of HTFA, HBZA, HDBM, HDPM and HACA were prepared by methods cited in the literature. The vanadyl complex of *p,p'*-dimethoxydibenzoylmethane was prepared by an analogous method to that used for $VO(DBM)_2$.
The vanadyl complex of HPTA was synthesized by an analogous method to that used for $VO(TFA)_2$. The HPTA was synthesized by condensation of pinacolone with ethyl trifluoro-acetate. The complexes were all filtered at the pump, washed with water and dried over silica gel (20^0/0.2 mm Hg). The complexes $VO(ACA)_2$, $VO(DPM)_2$, $VO(TFA)_2$ and $VO(PTA)_2$ were purified by vacuum sublimation at elevated temperatures.

methanol (10 ml). This solution was heated on a water bath (15 min) and set aside (24 hr). The resulting complexes were filtered at the pump, washed with methanol and air dried.

An alternative method used to prepare primary aliphatic amine adducts of $Ni(ACA)_2$ has been reported.[73] This consists of mixing molar proportions of nickel(II) chloride, acetylaceton and amine, dissolved in methanol. This method was attempted for the preparation of the substituted pyridine adducts but it was found that the product of the reaction consisted of the substituted pyridine complex of nickel(II) chloride only.

r. Primary Aliphatic Amine Adducts of Cobalt Acetylacetonate [71,74,98]

These complexes were prepared from cobalt(II) acetylacetonate dihydrate, which was prepared by a similar method to that for the analogous nickel(II) complex.

$[Co(ACA)_2(H_2O)_2]$ (1 gm, 1 mole) was dissolved in methanol (20 ml) with the aid of heat and the primary aliphatic amine (2 mole) added. The solution was set aside (1 hr) and the complex thus formed was filtered at the pump, washed with methanol and air dried.

The ammonia adduct was prepared by bubbling gaseous ammonia through a methanolic solution of cobalt(II) acetylacetonate dihydrate.

The aniline adduct was prepared by recrystallizing cobalt(II) acetylacetonate dihydrate from aniline, filtering at the pump and air drying.

III. RESULTS

1. ANALYSES AND PHYSICAL CHARACTERISTICS OF COMPLEXES

a. Hydrated Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot H_2O$

L	Colour	m.p.(°)	Calculated			Found		
			%C	%H	%U	%C	%H	%U
ACA	Yellow	d.[a]	24.7	3.3	49.0	24.7	3.3	48.9
TFA	Yellow	d.	20.2	1.7	40.1	20.7	1.9	39.8
BZA	Orange	d.	39.4	3.3	39.0	38.8	3.3	38.7
DBM	Red	d.	49.1	3.3	32.4	49.1	3.3	31.9
DPM	Red	d.	40.4	6.2	36.4	40.4	6.2	36.2
p-MeODBM	Red	d.	47.8	3.8	27.8	48.1	3.9	27.1

b. Anhydrous Uranyl β-Ketoenolates

$UO_2(L)_2$

L	Colour	m.p.(°)	Calculated			Found		
			%C	%H	%U	%C	%H	%U
ACA	Orange	d.	25.7	3.0	50.8	24.3	2.9	50.8
BZA	Brown	d.	40.6	3.1	40.2	40.1	3.0	39.9
DBM	Brown	d.	50.3	3.1	33.3	49.6	3.2	33.0

[a]Decomposition occurs over a wide temperature range.

c. Pyridine Adducts of Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot py$

L	Colour	m.p.(°)	Calculated				Found			
			%C	%H	%N	%U	%C	%H	%N	%U
ACA	Orange	d.	32.9	3.5	2.6	43.5	32.9	3.6	2.5	43.3
TFA	Yellow	174-177	27.5	2.0	2.1	36.3	27.0	2.3	1.9	36.5
BZA	Orange	196-200	44.7	3.5	2.1	35.5	44.9	3.5	2.1	35.0
DBM	Orange	d.	52.8	3.4	1.8	29.9	53.0	3.4	1.9	29.5
DPM	Orange	d.	45.3	6.1	2.0	33.3	45.3	6.0	1.9	33.0
PVA	Orange	122-125	39.9	5.0	2.2	37.7	40.2	4.9	2.2	37.5
EAA	Orange	d.	33.6	3.8	2.3	39.2	33.2	3.7	2.2	39.0
MAC	Red	153-156	35.5	4.0	2.4	41.4	35.2	3.8	2.4	41.0

d. Pyridine N-Oxide Adducts of Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot pyNO$

L	Colour	m.p.(°)	Calculated				Found			
			%C	%H	%N	%U	%C	%H	%N	%U
ACA	Orange	222-225	32.0	3.4	2.5	42.3	32.3	3.4	2.4	42.0
TFA	Yellow	132-135	26.8	2.0	2.1	35.5	27.1	1.9	2.1	35.5
BZA	Orange	200-203	43.7	3.4	2.0	34.6	43.7	3.2	1.9	34.3
DBM	Orange	210-213	51.8	3.4	1.7	29.3	51.3	3.3	1.8	29.1
DPM	Orange	241-244	44.3	5.9	1.9	32.5	44.2	5.9	1.7	32.4

e. Pyridine Adducts of Uranyl *o*-Hydroxyarylcarbonyl Compounds

$UO_2(L)_2 \cdot py$

L	Colour	m.p.(°)	Calculated %C	%H	%N	%U	Found %C	%H	%N	%U
ESAL	Orange	144-146	40.7	3.4	2.1	35.0	40.6	3.3	2.0	34.9
MSAL	Red	191-193	38.7	2.9	2.2	36.5	39.0	2.9	2.2	36.2
HPP	Red	167-170	42.6	3.6	2.2	36.8	41.9	3.8	2.1	36.6
BSAL	Orange	122-125	49.3	3.4	1.7	29.6	46.7	3.4	1.8	29.1
SAL	Red	119-122	38.6	2.6	2.4	40.3	39.2	2.6	2.4	40.0

f. Substituted Pyridine Adducts of Uranyl Dibenzoylmethanate

$UO_2(DBM)_2 \cdot R\text{-}C_5H_4N$

R	Colour	m.p.(°)	Calculated %C	%H	%N	%U	Found %C	%H	%N	%U
4-CH_3	Orange	d.	53.4	3.6	1.7	29.4	53.7	3.5	1.7	29.8
4-CN	Orange	d.	52.7	3.2	3.4	29.0	52.7	3.2	3.4	29.0
4-NH_2	Orange	d.	51.9	3.5	3.5	29.4	52.7	3.6	3.6	29.0
4-$CO_2C_2H_5$	Red	d.	52.6	3.6	1.6	27.4	53.0	3.4	1.7	27.5

h. Substituted Pyridine Adducts of Uranyl Benzoylacetonate

$UO_2(BZA)_2 \cdot R\text{-}C_5H_4N$

R	Colour	m.p.(°)	Calculated %C	%H	%N	%U	Found %C	%H	%N	%U
4-CH_3	Orange	d.	45.6	3.7	2.0	34.7	45.8	4.0	2.2	35.0
4-CN	Orange	d.	44.8	3.2	4.0	34.2	45.2	3.1	4.0	34.6
4-NH_2	Orange	d.	43.7	3.5	4.1	34.7	42.1	3.4	4.3	34.5
4-$CO_2C_2H_5$	Orange	d.	45.2	3.7	1.9	32.0	44.8	3.3	2.1	32.2

i. Substituted Pyridine Adducts of Uranyl Dipivaloylmethanate

$UO_2(DPM)_2 \cdot R\text{-}C_5H_4N$

R	Colour	m.p.(°)	Calculated %C	%H	%N	%U	Found %C	%H	%N	%U
4-CH_3	Orange	d.	46.1	6.2	1.9	32.6	44.9	6.0	2.3	25.1
4-CN	Orange	d.	45.4	5.7	3.8	32.1	41.5	5.3	4.2	29.5
4-NH_2	Orange	d.	44.4	6.1	3.8	32.6	41.6	5.6	4.4	31.9
4-$CO_2C_2H_5$	Orange	d.	45.7	6.0	1.8	31.2	45.3	5.9	1.9	30.9

j. Substituted Pyridine Complexes of Zinc Chloride

$ZnCl_2(R\text{-}C_5H_4N)_2$

R	Colour	m.p.(°)	Calculated %C	%H	%N	%Cl	Found %C	%H	%N	%Cl
H	White	191-193	40.8	3.4	9.5	24.1	40.6	3.6	9.0	24.0
4-CH_3	White	162-164	44.7	4.4	8.7	21.9	44.7	4.6	8.6	21.7
4-CN	White	199-202	41.8	2.3	16.3	20.6	41.7	2.6	15.9	20.5
4-$CO_2C_2H_5$	White	166-169	43.8	4.1	6.4	16.2	43.7	4.2	6.2	16.2

k. β-Ketoimines

$H_3C-CO-CH=C(CH_3)-NH-R$

R	b.p.(°)[a]	Calculated			Found		
		%C	%H	%N	%C	%H	%N
H	212-215	60.6	9.2	14.1	60.5	9.2	14.1
CH_3	206-209	63.7	9.8	12.4	63.7	9.8	12.4
C_2H_5	115-116	66.1	10.3	11.0	65.9	10.0	10.9
n-C_3H_7	221-223	68.0	10.7	9.9	68.1	10.6	9.9
i-C_3H_7	216-219	68.0	10.7	9.9	68.0	10.5	9.8
n-C_4H_9	241-244	69.6	11.0	9.0	69.6	11.1	9.0
s-C_4H_9	225-228	69.6	11.0	9.0	69.6	11.0	8.9
i-C_4H_9	231-234	69.6	11.0	9.0	69.4	10.9	8.9
t-C_4H_9	221-224	69.6	11.0	9.0	69.6	11.0	8.9
C_6H_{11}	279-282	72.9	10.6	7.7	73.0	10.7	7.6
C_6H_5	281-284	75.4	7.5	8.0	75.4	7.5	8.1
$CH_2C_6H_5$	299-301	76.2	8.0	7.4	75.8	7.8	7.1
$CH_2CH_2C_6H_5$	307-310	76.8	8.4	6.9	76.1	8.1	6.5
di-CH_3	256-259	66.1	10.3	11.0	66.0	10.1	10.8
di-C_2H_5	264-266	69.6	11.0	9.0	69.8	10.9	9.0

[a] at 760 mm Hg.

1. β-Ketoimine Adducts of Uranyl Acetylacetonate

$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)\text{-}NHR$

R	Colour	m.p.(°)	Calculated				Found			
			%C	%H	%N	%U	%C	%H	%N	%U
H	Orange	d.	31.7	4.1	2.5	41.9	31.8	4.2	2.5	41.7
CH_3	Orange	d.	33.1	4.3	2.4	40.9	33.0	4.4	2.4	40.6
C_2H_5	Orange	d.	34.3	4.6	2.4	40.0	34.3	4.6	2.5	39.7
n-C_3H_7	Orange	d.	35.5	4.8	2.3	39.1	35.7	4.8	2.3	38.7
i-C_3H_7	Orange	d.	35.5	4.8	2.3	39.1	35.5	4.7	2.5	38.7
n-C_4H_9	Orange	d.	36.6	5.0	2.3	38.2	36.6	5.2	2.3	38.0
s-C_4H_9	Orange	d.	36.6	5.0	2.3	38.2	36.6	4.9	2.3	37.9
i-C_4H_9	Orange	d.	36.6	5.0	2.3	38.2	36.5	4.9	2.3	37.9
t-C_4H_9	Orange	d.	36.6	5.0	2.3	38.2	36.7	5.1	2.4	38.0
C_6H_5	Orange	d.	39.2	4.2	2.2	37.0	39.4	4.2	2.3	36.7
di-CH_3	Orange	d.	34.3	4.6	2.4	40.0	34.7	4.6	2.5	39.7
di-C_2H_5	Orange	d.	36.6	5.0	2.3	38.2	36.5	5.0	2.3	38.0

m. Primary Aliphatic Amine Adducts of Uranyl Dibenzoylmethanate

$UO_2(DBM)_2 \cdot RNH_2$

R	Colour	m.p.(°)	Calculated				Found			
			%C	%H	%N	%U	%C	%H	%N	%U
H	Red	d.	49.1	3.4	1.9	32.5	49.3	3.3	2.1	33.0
CH_3	Red	d.	49.8	3.6	1.9	31.8	50.4	3.7	1.7	31.8
C_2H_5	Orange	d.	50.5	3.8	1.8	31.3	50.7	3.8	2.0	31.3
$n\text{-}C_3H_7$	Orange	d.	51.1	4.0	1.8	30.7	51.7	4.1	1.9	30.4
$i\text{-}C_3H_7$	Orange	d.	51.1	4.0	1.8	30.7	51.2	3.9	2.0	30.0
$n\text{-}C_4H_9$	Orange	d.	51.7	4.2	1.8	30.1	51.9	4.2	1.8	30.0
$s\text{-}C_4H_9$	Orange	d.	51.7	4.2	1.8	30.1	51.7	4.5	1.7	30.2
$i\text{-}C_4H_9$	Orange	d.	51.7	4.2	1.8	30.1	52.1	4.2	1.8	30.1
$t\text{-}C_4H_9$	Red	d.	51.7	4.2	1.8	30.1	51.8	4.2	1.8	29.8
C_6H_{11}	Red	d.	53.1	4.2	1.7	29.2	53.5	4.5	2.0	28.7
C_6H_5	Red	d.	53.4	3.6	1.7	29.4	53.1	4.0	1.7	29.1
$CH_2C_6H_5$	Red	d.	54.0	3.8	1.7	28.9	54.7	4.0	2.0	28.0
$CH_2CH_2C_6H_5$	Orange	d.	54.5	4.0	1.7	28.4	54.6	4.0	1.7	28.5

n. Primary Aliphatic Amine Adducts of Uranyl *p,p'*-Dimethoxydibenzoylmethanate

$UO_2(p\text{-}MeODBM)_2 \cdot RNH_2$

R	Colour	m.p.(°)	Calculated				Found			
			%C	%H	%N	%U	%C	%H	%N	%U
CH_3	Orange	d.	48.6	3.7	1.6	27.5	48.7	3.7	1.8	27.0
$t\text{-}C_4H_9$	Orange	d.	50.2	4.5	1.5	26.2	49.6	4.1	1.4	26.1
C_6H_5	Red	d.	51.7	4.0	1.5	25.6	51.3	3.7	1.6	25.1
$CH_2C_6H_5$	Red	d.	52.2	4.2	1.5	25.2	52.3	4.1	1.4	24.9

o. Anhydrous Vanadyl β-Ketoenolates

$VO(L)_2$

L	Colour	m.p.(°)	Calculated %C	Calculated %H	Found %C	Found %H
ACA	Blue	s.	45.3	5.3	45.8	5.6
TFA	Green	s.	32.2	2.2	32.4	2.1
BZA	Green	211-214	61.7	4.7	61.8	4.6
DBM	Green	264-267	70.2	4.3	70.3	4.5
DPM	Green	s.	61.0	8.8	61.2	8.8
PTA	Green	s.	42.0	4.4	41.7	4.5
p-MeODBM	Green	256-259	64.5	4.8	64.8	4.8

p. Substituted Pyridine Adducts of Vanadyl Acetylacetonate

$VO(ACA)_2 \cdot R\text{-}C_5H_4N$

R	Colour	m.p.(°)	Calculated %C	Calculated %H	Calculated %N	Found %C	Found %H	Found %N
4-C_2H_5	Green	d.[a]	54.8	6.2	3.7	55.0	6.2	4.0
4-C_6H_5	Green	d.	60.0	5.5	3.3	60.2	5.4	3.4
4-CH_3	Green	d.	53.6	5.9	3.9	53.9	5.8	4.0
4-COC_6H_5	Green	d.	58.9	5.1	3.1	59.1	5.6	3.3
4-n-C_3H_7	Green	d.	55.9	6.5	3.6	55.8	6.4	3.7
4-$CO_2C_2H_5$	Khaki	d.	51.9	5.5	3.3	51.5	5.9	3.6
4-$N(CH_3)_2$	Green	d.	52.7	6.2	7.2	52.8	6.4	7.3
4-t-C_4H_9	Green	d.	57.0	6.8	3.5	56.7	6.7	3.5
4-CN	Green	d.	52.0	4.9	7.6	52.0	5.2	7.5
H	Green	d.	52.3	5.6	4.0	52.5	5.5	4.1
4-NH_2	Emerald	d.	50.2	5.6	7.8	50.0	5.8	7.8
3,5-di-CH_3	Green	d.	54.8	6.2	3.7	54.6	6.6	4.0
3,4-di-CH_3	Green	d.	54.8	6.2	3.7	54.7	6.3	4.0
3-NH_2	Green	d.	50.2	5.6	7.8	49.9	5.7	7.7

[a] All complexes appeared to lose the adducted pyridine at 100-150°, the remaining solid then sublimed.

q. Substituted Pyridine Adducts of Nickel Acetylacetonate

$[Ni(ACA)_2(R\text{-}C_5H_4N)_2]$

R	Colour	m.p.(°)[a]	Calculated			Found		
			%C	%H	%N	%C	%H	%N
4-CH_3	Blue	d.	59.6	6.4	6.3	59.0	6.6	6.3
4-CN	Khaki	d.	56.8	4.8	12.1	56.9	4.9	12.3
4-$COCH_3$	Green	d.	57.7	5.7	5.6	57.6	5.5	5.7
4-$CO_2C_2H_5$	Green	d.	55.8	5.8	5.0	56.0	5.7	5.0
H	Purple	d.	57.9	5.8	6.7	57.8	5.9	6.8
3,4-di-CH_3	Blue	d.	61.2	6.8	6.0	60.9	7.0	6.1
4-t-C_4H_9	Blue	d.	63.8	7.7	5.3	63.6	7.4	5.5
4-$N(CH_3)_2$	Blue	d.	57.5	6.8	11.2	57.4	6.9	11.1
4-COC_6H_5	Green	d.	65.6	5.2	4.5	65.8	5.1	4.5
4-C_6H_5	Blue	d.	67.8	5.7	4.9	67.4	5.6	5.0
3-CN	Blue	d.	56.8	4.8	12.1	57.0	4.8	11.9
3,5-di-Cl	Grey	d.	43.4	3.7	5.1	43.5	3.5	5.1[b]
3-I	Purple	d.	36.0	3.3	4.2	35.8	3.2	4.2[c]
3-Br	Purple	d.	41.9	3.9	4.9	42.1	3.9	5.1[d]
3-COC_6H_5	Blue	d.	65.6	5.2	4.5	65.4	5.1	4.7
3,5-di-CH_3	Blue	d.	61.2	6.8	5.9	61.2	6.8	5.9
3-C_2H_5	Blue	d.	61.2	6.8	5.9	61.2	6.8	6.0
4-CO_2CH_3	Green	d.	54.3	5.3	5.3	54.2	5.2	5.3
4-n-C_3H_7	Blue	d.	62.5	7.3	5.6	62.5	7.1	5.6
3-$CO_2C_2H_5$	Blue	d.	55.8	5.8	5.0	55.7	5.6	5.1
4-C_2H_5	Blue	d.	61.2	6.8	6.0	61.2	6.8	5.6
4-$CH_2C_6H_5$	Blue	d.	68.6	6.1	4.7	68.2	5.8	4.9
3-CO_2CH_3	Blue	d.	54.3	5.3	5.3	54.5	5.3	5.3
3-$COCH_3$	Blue	d.	57.7	5.7	5.6	57.8	5.7	5.6

[a] All complexes appeared to lose the adducted pyridine at 100-150° leaving a charred mass which then slowly melted at about 250°.

[b] Cl calc. 25.7%; found 25.7%.

[c] I calc. 38.1%; found 38.0%

[d] Br calc. 27.9%; found 27.5%.

r. Primary Aliphatic Amine Adducts of Cobalt Acetylacetonate

$$\left[Co(ACA)_2(R\text{-}NH_2)_2\right]$$

R	Colour	m.p.(°)[a]	Calculated			Found		
			%C	%H	%N	%C	%H	%N
H	Pink	151-154	41.2	6.9	9.6	39.9	6.8	9.6
C_2H_5	Pink	125-145	48.4	8.1	8.1	47.8	7.7	8.1
n-C_3H_7	Pink	131-133	51.2	8.6	7.5	50.9	8.3	7.0
i-C_3H_7	Pink	116-119	51.2	8.6	7.5	50.9	9.0	8.1
n-C_4H_9	Pink	142-145	53.6	9.0	6.9	53.4	8.9	6.9
s-C_4H_9	Pink	112-114	53.6	9.0	6.9	53.0	8.9	6.7
i-C_4H_9	Pink	136-139	53.6	9.0	6.9	52.9	8.6	7.8
C_6H_{11}	Pink	131-134	58.3	8.5	6.2	57.9	9.2	6.1
C_6H_5	Pink	129-132	59.6	6.4	6.3	58.8	6.3	6.4
$CH_2C_6H_5$	Pink	181-185	61.1	6.8	5.9	60.7	6.8	6.0
$CH_2CH_2C_6H_5$	Pink	171-174	62.5	7.3	5.6	62.2	7.2	5.5

[a] These complexes all sublimed at approximately 10° below their melting points.

2. INFRARED RESULTS

All values are cm^{-1}

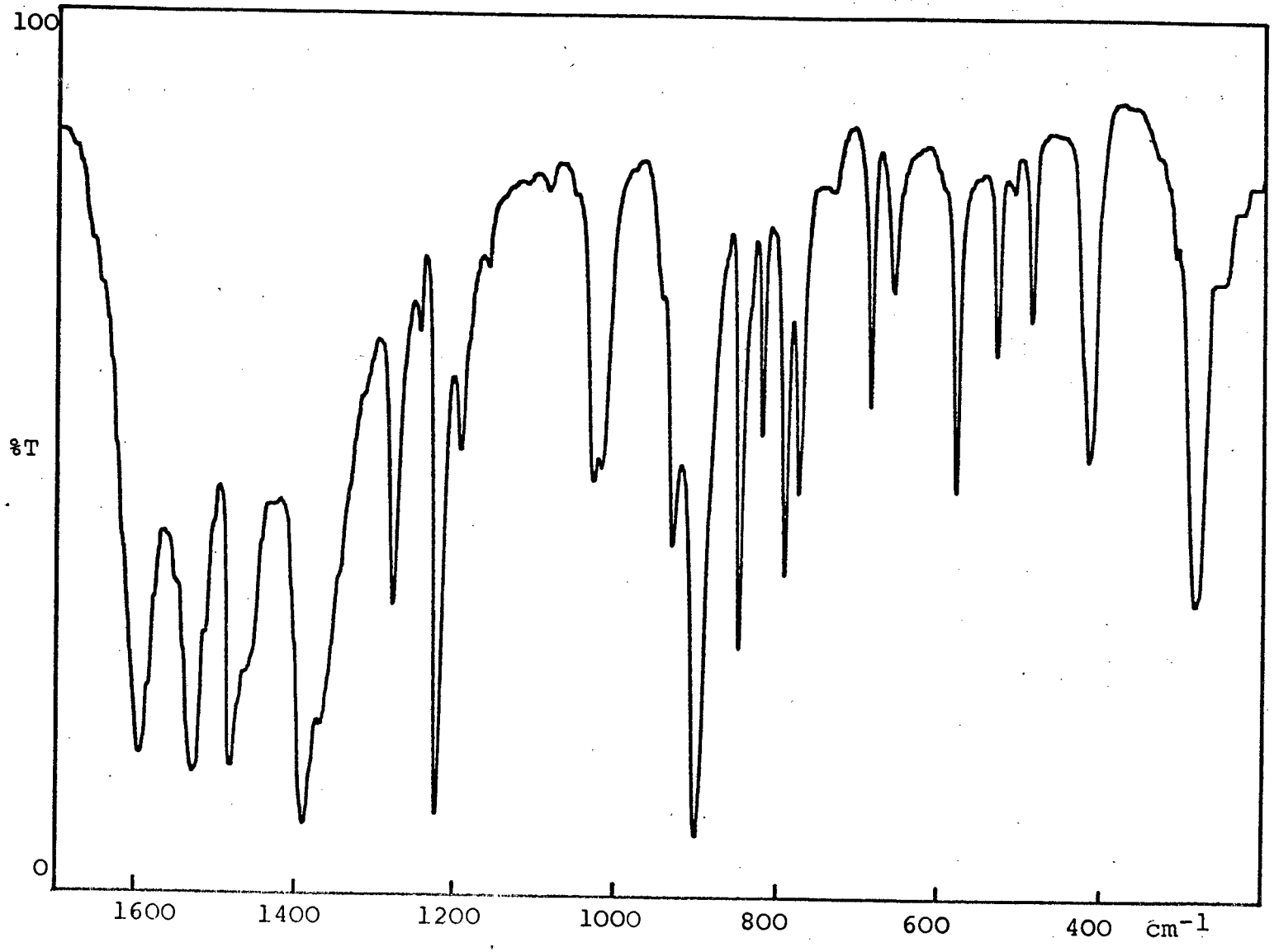
a. Various Adducts of Uranyl Acetylacetonate

$UO_2(ACA)_2 \cdot X$

X	Nil	H_2O	pyNO	py	4-CH_3 C_5H_4N	4-CN C_5H_4N	4-NH_2 C_5H_4N	4-$CO_2C_2H_5$ C_5H_4N
Assignment								
νC=O	1565	1583	1585	1570	1572	1570	1582	1571
νC=C	1522	1525	1518	1527	1529	1527	1528	1528
δC=C + νC-CH_3	1264	1274	1272	1274	1272	1274	1270	1274
CH_3 rock	1026	1035	1025	1026	1021	1024	1013	1023
νC=O + νC-CH_3	-	929	927	925	925	926	929	926
νU=O asym	928	922	896	913	909	909	894	910
δC-H o.o.p.	780	783	770	796	805	802	781	802
Ring def.	647	652	654	653	655	648	655	650
νU-O	528	529	524	523	524	523	522	524
νU-O + νC-CH_3	403	404	403	403	404	403	410	403
δO=U=O	275	269	272	273	281	280	271	281

Fig. 1.

Infrared Spectrum of $UO_2(ACA)_2 \cdot pyNO$



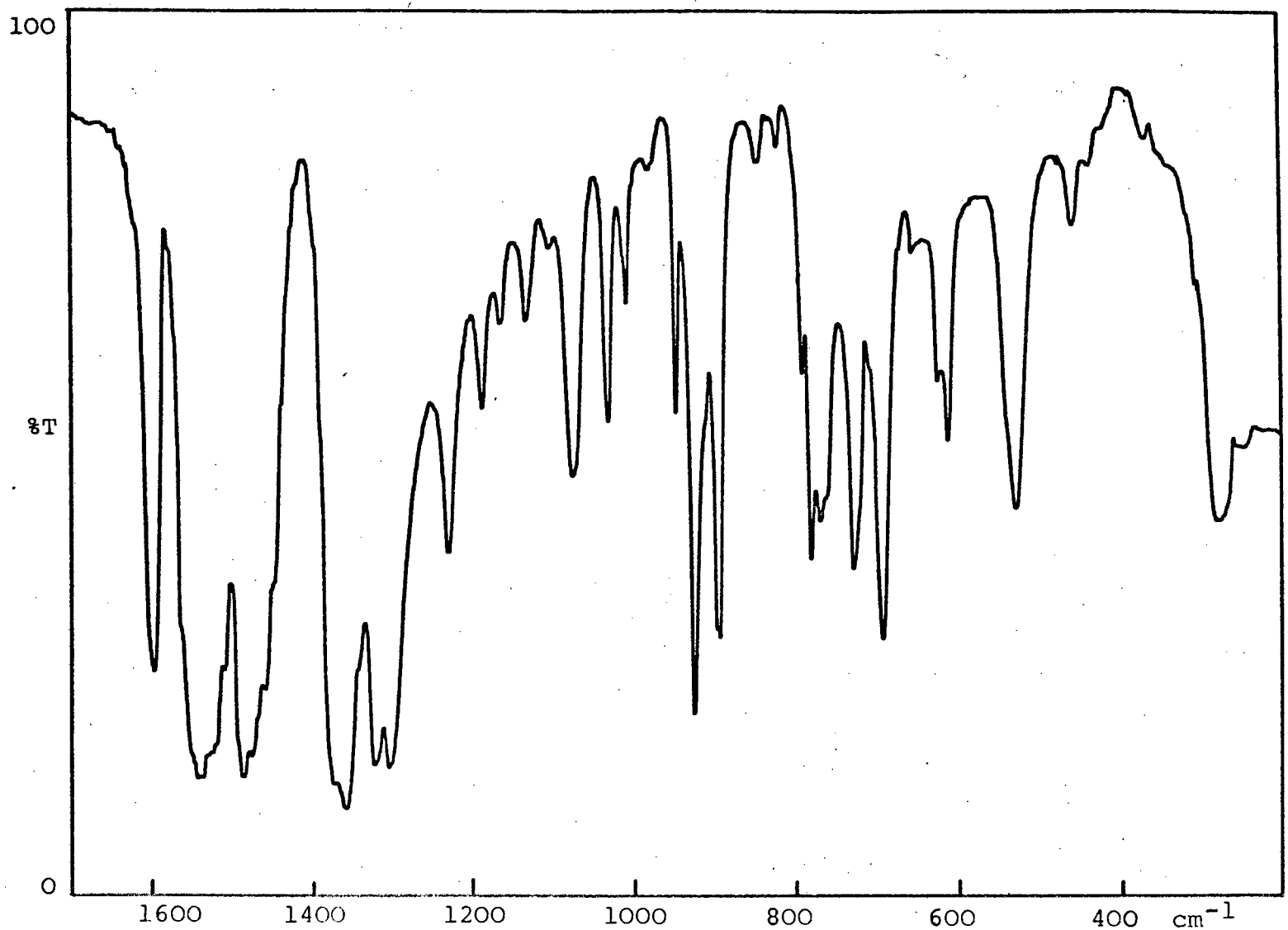
b. Various Adducts of Uranyl Dibenzoylmethanate

$UO_2(DBM)_2 \cdot X$

X	Nil	H_2O	pyNO	py	4-CH_3 C_5H_4N	4-NH_2 C_5H_4N	4-CN C_5H_4N	4-$CO_2C_2H_5$ C_5H_4N
Assignment								
Phenyl	1595	1593	1593	1591	1594	1594	1593	1595
νC=O	1541	1540	1542	1539	1544	1544	1540	1545
νC=C	1522	1519	1525	1522	1528	1526	1526	1529
νC=C +	1316	1315	1315	1315	1318	1320	1317	1317
νC-Ph	1295	1301	1302	1291	1303	1305	1301	1295
δC-H i.p.	1224	1225	1223	1225	1228	1224	1225	1226
νC-Ph	941	942	943	941	942	942	942	942
νU=O asym.	904	915	898	909	905	895	907	906
δC-H o.o.p.	815	810	815	813	811	817	826	828
	784	785	783	785	789	790	789	791
	761	756	752	747	759	759	756	750
Substitution	720	714	722	716	723	725	723	728
Patterns	685	685	688	684	686	688	686	686
	606	605	605	605	607	607	606	608
νU-O	525	523	523	524	524	521	522	523
νU-O + νC-Ph	451	451	454	453	452	454	-	455
δO-U-O	430	432	426	428	437	433	433	433
δO=U=O	269	269	261	269	272	267	279	271

Fig. 2.

Infrared Spectrum of $UO_2(DBM)_2$



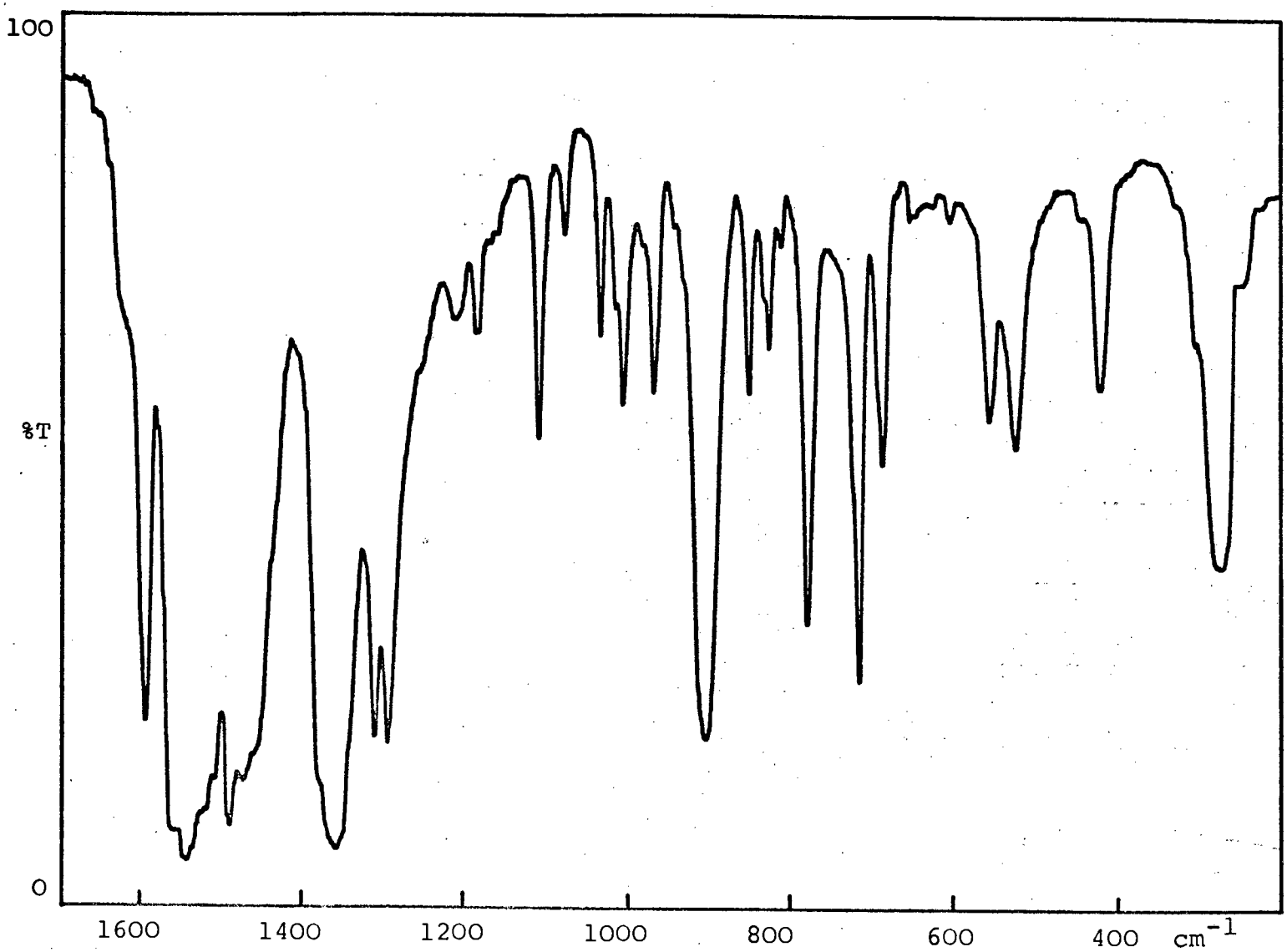
c. Various Adducts of Uranyl Benzoylacetonate

$UO_2(BZA)_2 \cdot X$

X	Nil	H_2O	pyNO	py	4-CH_3 C_5H_4N	4-CN C_5H_4N	4-NH_2 C_5H_4N	4-$CO_2C_2H_5$ C_5H_4N
Assignment								
Phenyl	1591	1594	1592	1590	1600	1594	1594	1595
νC=O	1552	1561	1560	1555	1559	1564	1551	1555
νC=C	1531	1533	1519	1533	1536	-	1523	1534
Phenyl	1487	1488	1487	1488	1490	-	-	1491
νC=C + $\nu C-CH_3$	1290	1290	1290	1288	1297	1292	1288	1295
δC-H i.p.	1209	1209	1208	-	1216	1214	1222	-
CH_3 rock	1029	1030	1030	1026	1026	1034	1015	1032
νC=O + $\nu C-CH_3$	961	964	960	963	965	963	964	964
νU=O asym.	918	919	905	911	917	908	914	911
δC-H o.o.p	848	847	847	849	849	850	849	849
	-	837	834	-	-	-	-	-
Substitution Patterns	768	768	776	765	765	780	767	765
	710	718	727	712	715	711	713	710
	680	680	674	679	687	681	687	686
νU-O	555	555	554	553	551	555	557	554
	528	521	522	524	523	521	519	521
νU-O + $\nu C-CH_3$	413	412	411	412	418	409	415	414
δO=U=O	270	269	260	267	267	263	263	265

Fig. 3.

Infrared Spectrum of $UO_2(BZA)_2 \cdot H_2O$



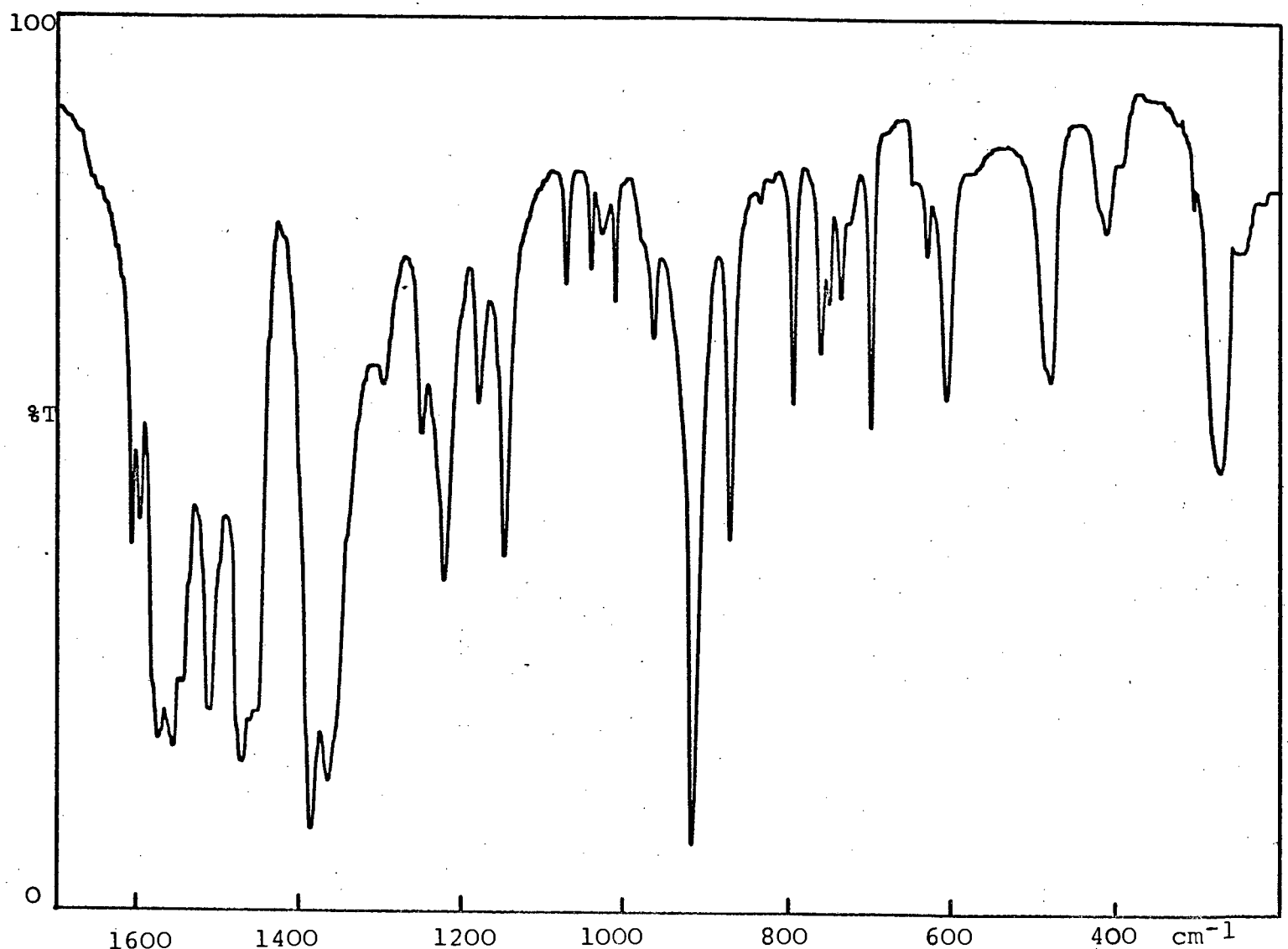
d. Various Adducts of Uranyl Dipivaloylmethanate

$UO_2(DPM)_2 \cdot X$

X	H_2O	pyNO	py	4-CH_3 C_5H_4N	4-CN C_5H_4N	4-NH_2 C_5H_4N	4-$CO_2C_2H_5$ C_5H_4N
Assignment							
νC=O	1563	1570	1568	1569	1563	1564	1569
νC=O	1548	1550	1551	1550	1549	1548	1551
νC=C	1512	1506	1507	1506	1508	1512	1511
δC-H i.p.	1354	1359	1360	1359	1356	1358	1362
νC=C + νC-Bu	1294	1290	1294	1292	1295	1293	1280
	1250	1250	1248	1249	1250	1251	1251
$C(CH_3)_3$	1226	1235	1227	1223	1226	1233	1226
Skeletal	1179	1177	1179	1178	1178	1177	1178
	1144	1143	1146	1146	1146	1147	1146
CH_3 rock	1017	1021	1027	1023	1023	1013	1025
νC=O+ νC-Bu	962	964	964	965	964	967	964
νU=O asym.	908	903	917	916	913	893	911
	873	871	872	872	873	874	874
	826	822	836	826	829	834	834
δC-H o.o.p.	795	793	795	809	801	796	795
	762	761	762	761	771	766	765
	740	737	738	738	739	739	740
νU-O	608	605	607	607	608	608	607
νU-O +	488	485	486	493	489	488	488
ring def.	481	480	479	481	479	480	478
νU-O	413	409	409	407	411	410	413
δO=U=O	270	270	270	270	269	270	272

Fig. 4.

Infrared Spectrum of $UO_2(DPM)_2 \cdot py$



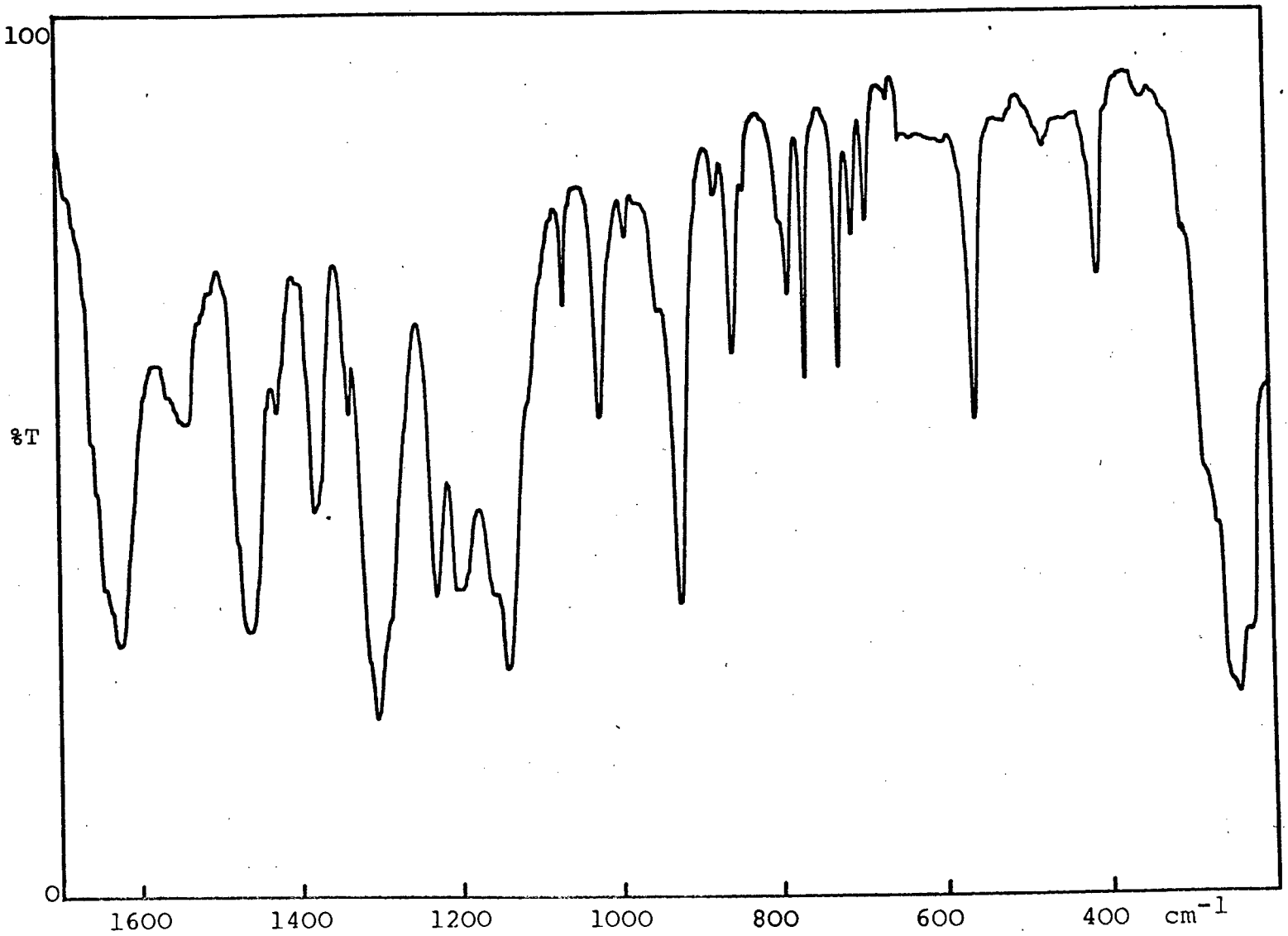
e. Various Adducts of Uranyl Trifluoroacetylacetonate

$UO_2(TFA)_2 \cdot X$

X	H_2O	pyNO	py	$4\text{-}CO_2C_2H_5C_5H_4N$
Assignment				
νC=O	1624	1620	1621	1622
νC=C	1534	1533	1538	1537
νC=C + $\nu C\text{-}CH_3$	1290	1301	1302	1299
CF_3	1232	1232	1226	1228
CF_3	1192	1193	1198	1202
CF_3	1155	1143	1146	1156
δC-H i.p.	1140	1134	1139	1139
CH_3 rock	1025	1017	1018	1024
νC=O + $\nu C\text{-}CH_3$	957	950	951	951
νU=O asym.	929	915	922	927
$\nu C\text{-}CF_3$	860	859	859	861
δC-H o.o.p.	801	781	787	789
$\nu C\text{-}CF_3$	728	727	728	728
νU-O	568	561	562	561
CF_3	520	519	518	518
νU-O + $\nu C\text{-}CH_3$	412	403	408	406
δO-U-O	295	317	329	272
δO=U=O	230	232	230	222

Fig. 5.

Infrared Spectrum of $UO_2(TFA)_2 \cdot 4\text{-}CO_2C_2H_5C_5H_4N$



f. Pyridine Adducts of Various Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot py$

Assignment	L= PVA	Assignment	L= EAA	Assignment	L= MAC
νC=O	1584	νC=O	1605	νC=O	1582
νC=C	1520	νC=C ?	1578	νC=C	-
νC=C + $\nu C-CH_3$	1290	νC=C ?	1515	νC=C +	1310
	1220	νC=C + $\nu C-CH_3$	1275	$\nu C-CH_3$	1299
$C(CH_3)_3$	1210	C-O-C	1265	δC-H i.p.	1177
skeletal	1168	δC-H i.p.	1175	CH_3 rock	981
	1153	CH_3 rock	1012	νU=O asym.	907
CH_3 rock	1029	νC=O + $\nu C-CH_3$	967	δC-H o.o.p.	763
νC=O + $\nu C-CH_3$	961	νU=O asym.	918	νU-O +	716
νU=O asym.	916	δC-H o.o.p.	795	ring def.	653
	884	νU-O + ring def	571	νU-O	555
	775	νU-O	456		541
δC-H o.o.p.	760	νU-O + $\nu C-CH_3$	423	νU-O + $\nu C-CH_3$	452
	702	δO-U-O	355	δO-U-O	427
νU-O	621	δO=U=O	272	δO=U=O	270
νU-O +	548				
ring def.	479				
νU-O	416				
δO=U=O	269				

Fig. 6.

Infrared Spectrum of $UO_2(PVA)_2 \cdot py$

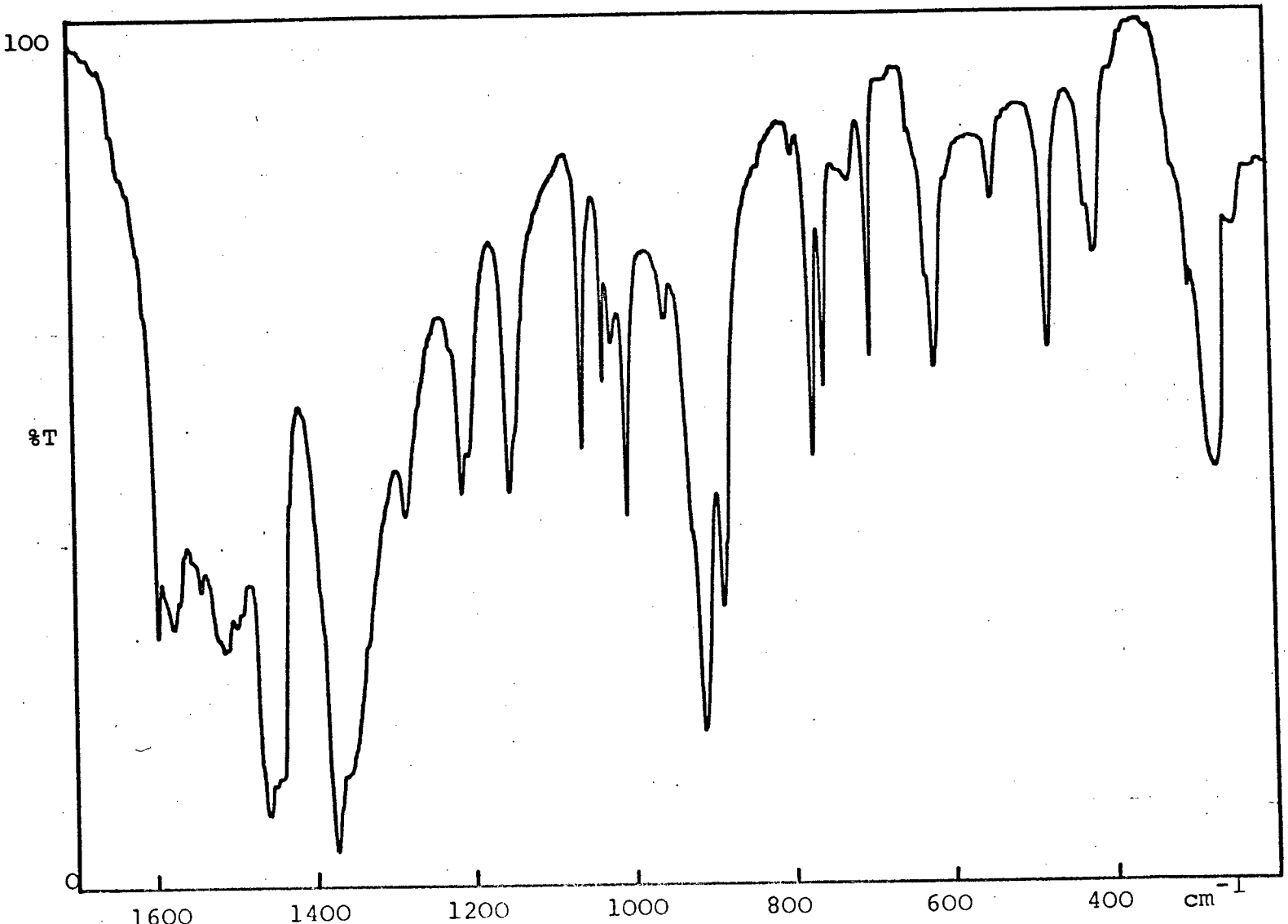
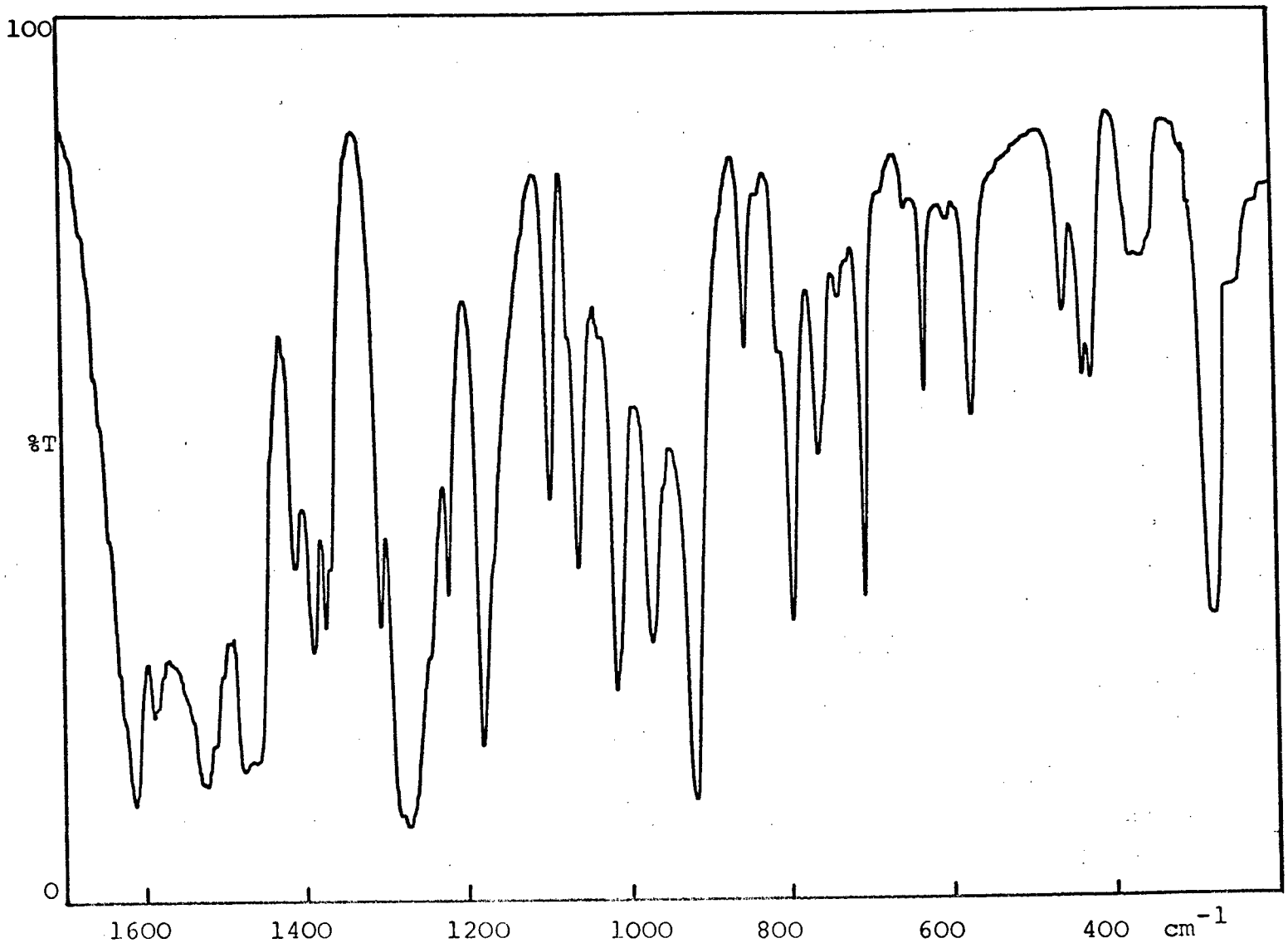


Fig. 7.

Infrared Spectrum of $UO_2(EAA)_2 \cdot py$



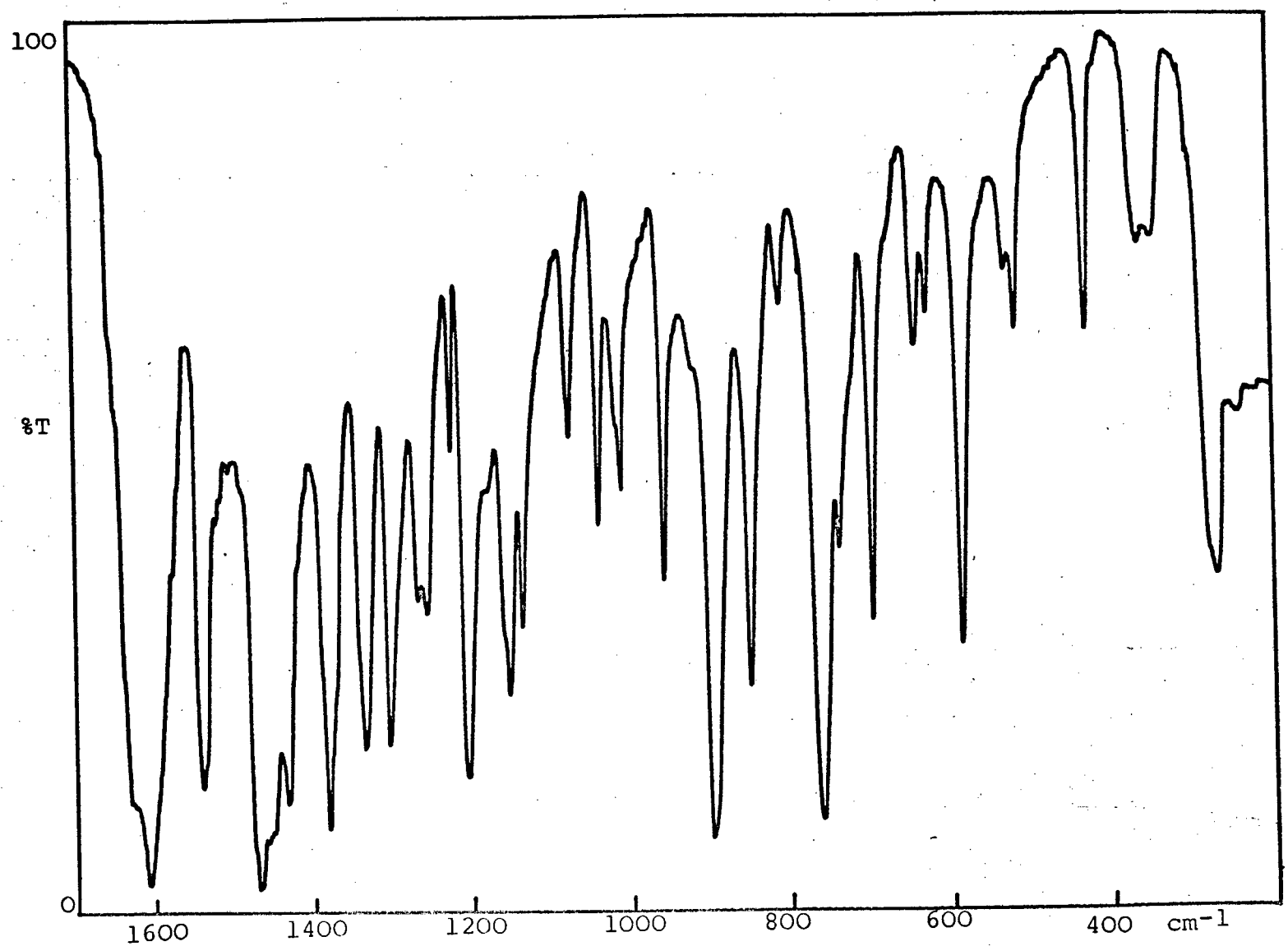
g. Pyridine Adducts of Uranyl o-Hydroxyarylcarbonyls

$UO_2(L)_2 \cdot py$

L	HPP	SAL	ESAL	MSAL	BSAL
Assignment					
νC=O	1628	1634	1643	1645	1656
νC=O	1607	1618	1631	1630	1639
νC=C	1538	1537	1548	1551	1550
?	1334	-	1335	1341	1326
?	1303	1312	1310	1317	1302
Phenyl ?	1268	1193	1261	1245	1248
	1256	1185	1238	1234	-
?	1206	1205	1199	1195	1213
Phenyl ?	1153	1149	1157	1156	1159
	1137	1125	1144	1142	1141
νC=O + νC-R	958	-	-	951	949
νU=O asym.	899	901	907	910	916
Ring Def.	645	660	662	665	665
νU-O ?	588	588	595	591	597
νU-O ?	535	542	551	555	565
Ring Def.	521	-	536	529	534
νU-O ?	431	467	413	431	491
δO-U-O ?	329	312	336	360	388
δO=U=O	263	259	258	261	251

Fig. 8.

Infrared Spectrum of $UO_2(HPP)_2 \cdot py$

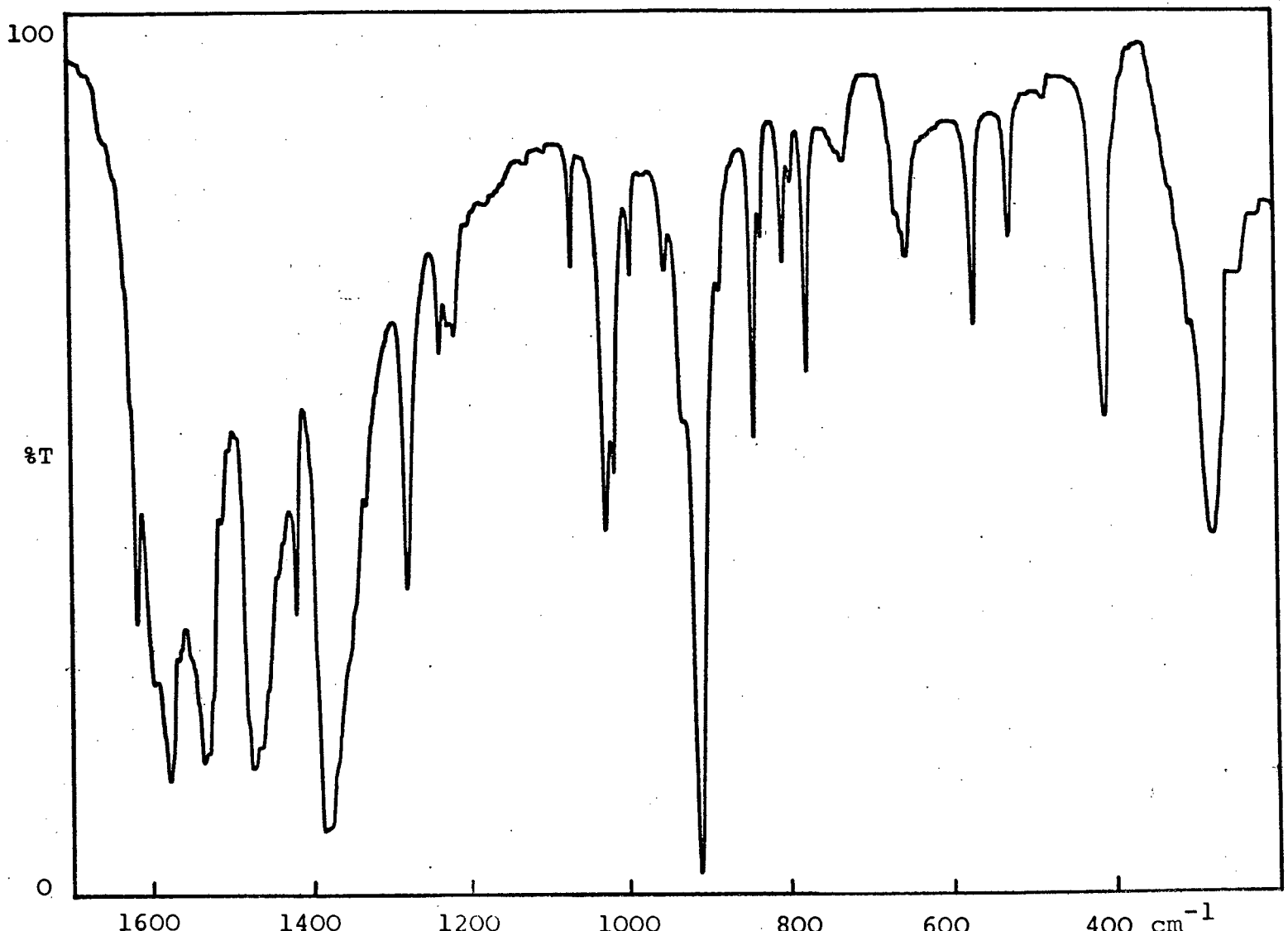


h. Substituted Pyridine Adducts of Uranyl Acetylacetonate $UO_2(ACA)_2 \cdot R\text{-}C_5H_4N$

R	σ x10²	νC=O	νC=C	δC=C + νC-CH₃	δC-H i.p.	CH₃ rock	νC=O + νC-CH₃	νU=O asym.	δC-H o.o.p.	Ring def.	νU-O	νU-O + νC-CH₃	δO=U=O
3-CN	+68	1567	1530	1273	1192	1020	926	909	806	650	523	402	271
4-CN	+63	1570	1527	1274	1214	1024	926	909	802	648	523	403	280
4-CO_2CH_3	-	1568	1533	1274	1197	1023	925	908	801	650	525	405	277
4-$CO_2C_2H_5$	+52	1571	1528	1274	-	1023	926	910	802	650	524	403	281
4-$COCH_3$	+52	1567	1527	1271	1196	1020	925	908	801	649	521	403	272
4-COC_6H_5	+46	1578	1530	1278	1197	1023	925	910	807	650	525	403	270
3-$CO_2C_2H_5$	+40	1572	1528	1275	1205	1023	925	910	801	644	523	404	276
3-Br	+38	1571	1529	1275	1197	1021	926	908	798	654	526	402	271
3-Cl	+37	1568	1531	1272	1197	1021	926	909	815	654	524	402	276
3-COC_6H_5	-	1586	1529	1271	1201	1024	929	908	803	655	524	403	271
3-$COCH_3$	+31	1567	1529	1274	1203	1024	927	908	801	658	521	403	273
4-C_6H_5	+ 1	1573	1530	1275	-	1020	925	910	799	653	522	403	273
H	0	1570	1527	1274	-	1026	925	913	796	653	523	403	273
3-CH_3	- 8	1585	1528	1272	1202	1022	927	909	809	652	523	404	271
4-$CH_2C_6H_5$	-	1575	1533	1274	1196	1025	931	908	800	650	523	403	272
4-n-C_3H_7	-13	1572	1524	1273	-	1018	925	910	795	655	523	404	273
3,5-di-CH_3	-14	1573	1531	1274	-	1024	929	907	799	657	522	404	271
4-C_2H_5	-15	1574	1526	1274	-	1020	924	910	799	656	524	404	272
3-NH_2	-16	1568	1527	1273	1198	1026	926	908	800	648	525	404	273
4-CH_3	-17	1572	1529	1272	-	1021	925	909	805	655	524	404	281
4-t-C_4H_9	-20	1584	1531	1274	1202	1022	927	910	784	655	525	404	274
3,4-di-CH_3	-24	1577	1530	1277	1204	1025	929	908	775	656	523	404	275
4-OH	-36	1587	1530	1271	1191	1021	931	898	771	655	524	408	272
4-NH_2	-66	1582	1528	1270	1193	1013	929	894	781	655	522	410	271
3,4-di-NH_2	-82	1582	1520	1267	1200	1021	930	890	782	651	524	413	271

Fig. 9.

Infrared Spectrum of $UO_2(ACA)_2 \cdot 4\text{-}CNC_5H_4N$



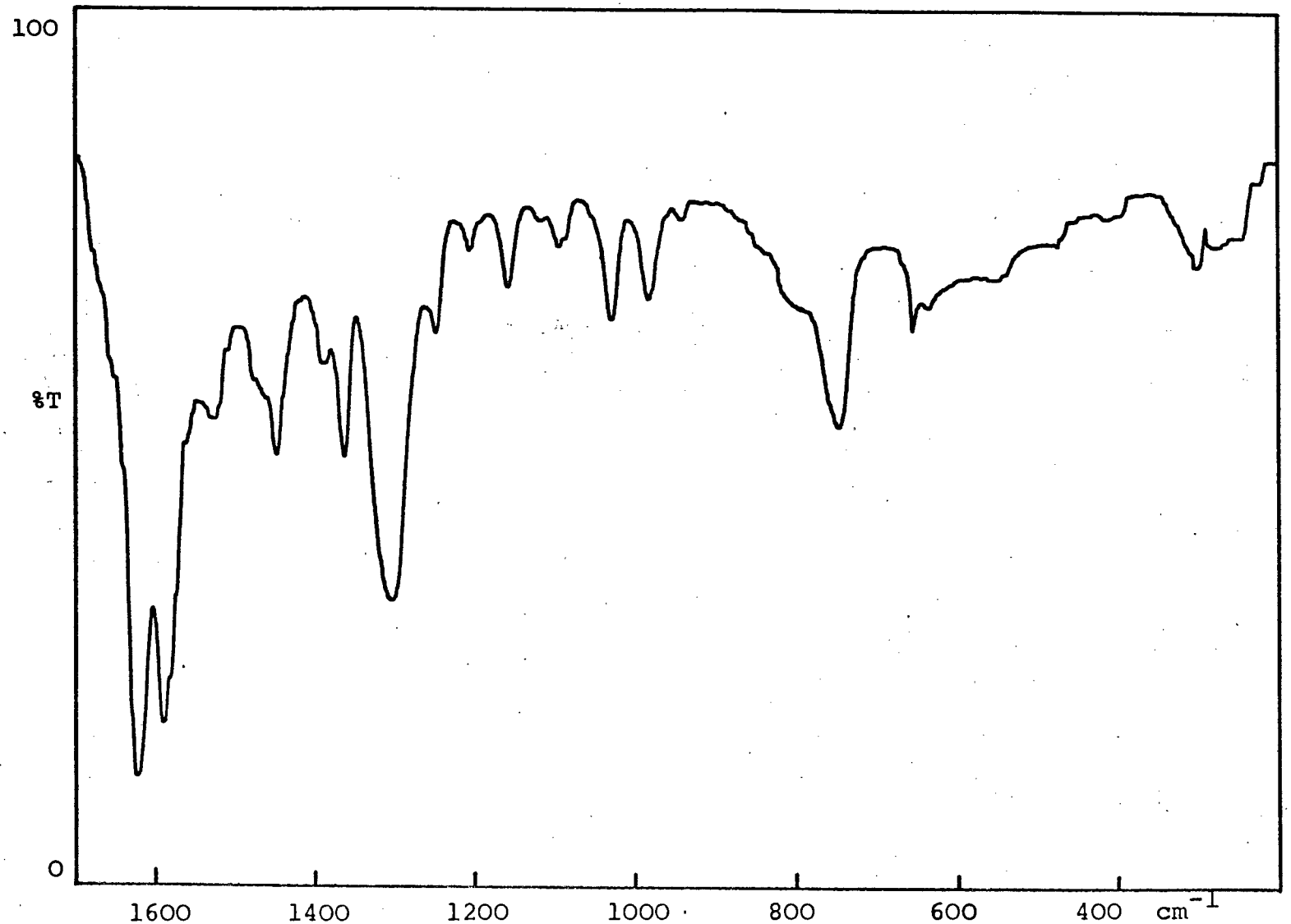
i. β-Ketoimines (liquid films)

$H_3C-CO-CH=C(CH_3)-NHR$

σ* x 10^3 and R	+600 C_6H_5	+490 H	+215 Bz	+80 β-PhEt	0 Me	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-150 Cx	-190 i-Pr	-210 s-Bu	-300 t-Bu	- di-Me	- di-Et
Assignment															
νN-H asym.	-	3358	-	-	-	-	-	-	-	-	-	-	-	-	-
νN-H sym.	-	3192	-	-	-	-	-	-	-	-	-	-	-	-	-
νC=O + δN-H	1625	1628	1621	1619	1618	1616	1617	1618	1620	1615	1619	1619	1615	1635	1640
νC=O	1606	1547	1581	1585	1585	1582	1585	1587	1583	1585	1584	1586	1599	1573	1556
νC=C	1580	-	1521	1527	1531	1531	1525	1524	1527	1522	1521	1526	1525	1550	1537
δC-H	-	1421	1460	1451	1449	1445	1445	1447	1450	1448	1440	1449	1446	1409	1450
δC-H	-	-	1383	1382	1384	1383	1386	-	1381	1381	1396	1383	1373	-	1383
δC-H	1360	1361	1360	1360	1358	1360	1359	1359	1357	1357	1361	1362	1359	1363	1360
δC=C +νC-CH_3	1280	1295	1303	1307	1309	1305	1303	1307	1306	1305	1310	1312	1330	1266	1290
?	1189	1197	-	1200	1163	1157	1154	1158	1155	1199	1172	1158	1240	1191	1190
?	1084	1108	1109	1110	1085	1067	1089	1096	1092	1112	1127	1134	1198	-	1080
CH_3 rock	1023	1024	1031	1020	1021	1022	1024	1024	1025	1025	1019	1022	1021	1021	1046
?	-	992	991	985	975	954	979	983	981	973	967	977	967	962	978
νC=O + νC-CH_3	924	-	938	932	944	933	931	937	939	933	937	933	936	-	956
?	908	899	-	-	-	-	879	-	899	892	887	860	-	-	802
?	824	-	-	-	837	783	794	-	790	802	794	805	811	-	-
δC-H o.o.p.	752	750	743	751	741	741	744	741	741	741	740	741	741	782	780
N-CH_2 ?	-	-	657	654	653	652	652	652	655	657	652	651	652	595	614
Ring def.	633	635	634	634	633	633	635	633	633	635	634	634	633	-	-
?	541	558	552	550	534	553	550	547	549	550	548	549	552	-	-
?	-	489	469	500	-	-	472	480	485	475	479	499	465	480	-
?	-	-	-	-	-	450	-	-	455	-	435	459	442	-	-
νC-CH_3	419	402	405	-	404	-	401	399	406	406	418	420	-	-	-
?	352	-	-	-	-	-	367	-	-	357	368	384	383	-	-

Fig. 10.

Infrared Spectrum of acetylacetone n-propylimine



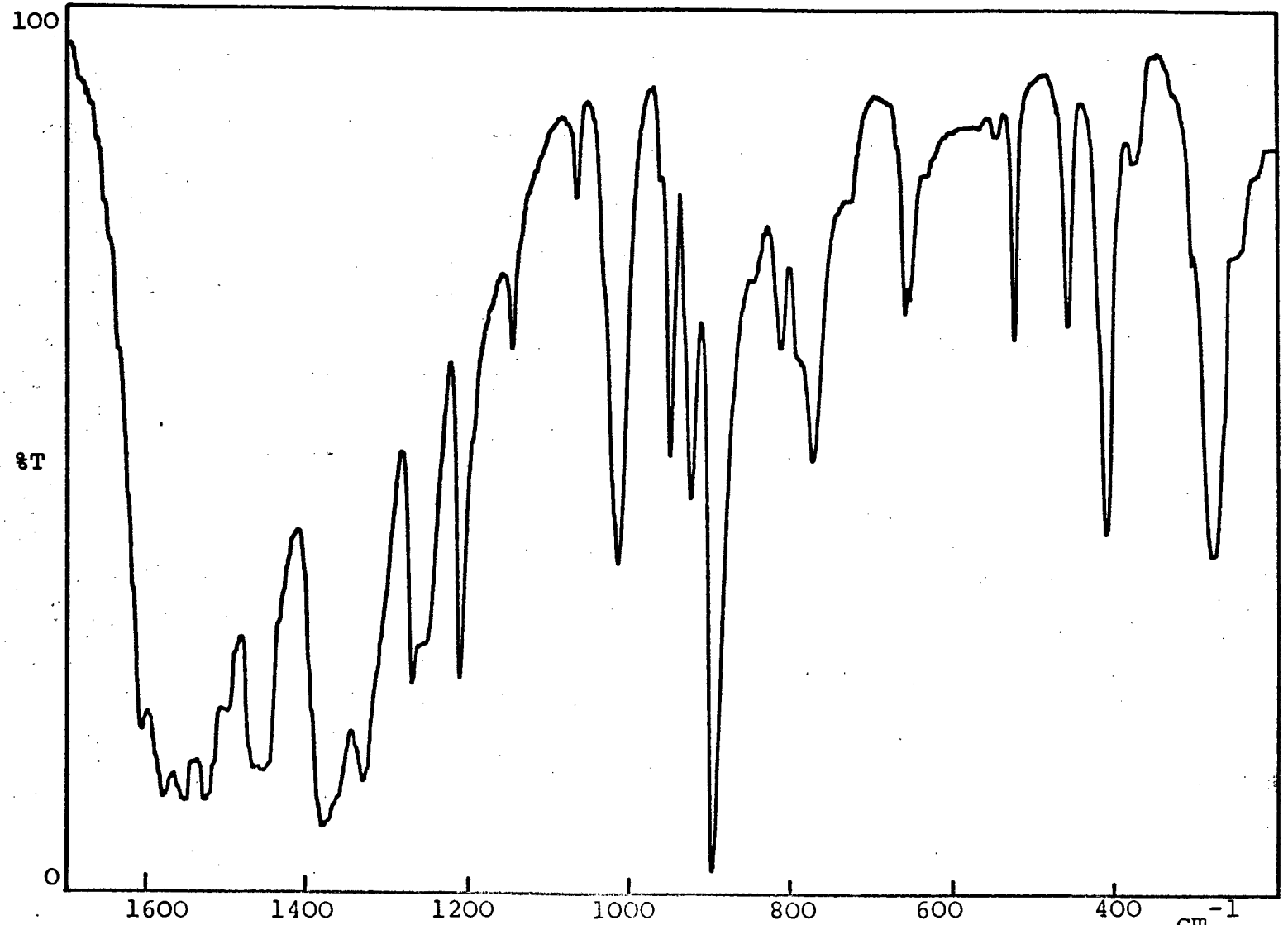
j. β-Ketoimine Adducts of Uranyl Acetylacetonate

$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)\text{-}NHR$

σ* x 10^3 and R	+600 C_6H_5	+490 H	0 Me	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-190 i-Pr	-210 s-Bu	-300 t-Bu	- di-Me	- di-Et	HACA adduct
Assignment													
νN-H asym.	-	3372	-	-	-	-	-	-	-	-	-	-	-
νN-H sym.	-	3214	-	-	-	-	-	-	-	-	-	-	-
δN-H	-	1645	-	-	-	-	-	-	-	-	-	-	-
νC=O	1615	1585	1612	1605	1608	1609	1611	1600	1609	1600	-	-	1612
νC=O	1583	1575	1578	1578	1575	1578	1576	1584	1587	1585	1587	1597	1577
νC=C	1551	1548	1551	1551	1560	1559	1556	1554	1555	1557	-	-	1530
νC=C	1522	1525	1527	1527	1522	1520	1522	1523	1532	1528	1525	1530	1520
νC-N	1328	1322	1330	1332	1338	1339	1339	1343	1347	1348	1352	1353	-
δC=C + $\nu C\text{-}CH_3$	1271	1270	1275	1271	1268	1270	1268	1269	1273	1270	1272	1270	1268
δC-H i.p.	1218	1219	1211	1213	1213	1215	1214	1210	1214	1219	1217	1230	-
?	1079	1094	1078	1067	1086	1092	1089	-	-	-	-	-	-
CH_3 rock	1022	1014	1022	1016	1018	1019	1015	1021	1025	1023	1023	1025	1019
?	957	952	951	952	959	956	958	954	959	954	977	973	947
νC=O + $\nu C\text{-}CH_3$	924	931	924	927	926	925	925	924	927	925	927	930	925
νU=O asym.	905	912	912	898	897	905	903	900	905	907	906	905	910
δC-H o.o.p.	793	795	798	814	807	-	800	799	800	792	792	805	815
	769	776	784	775	779	771	784	774	775	773	760	780	801
Ring def.	653	657	657	659	659	655	658	652	656	654	654	659	659
?	629	618	627	630	626	628	631	632	632	629	617	608	-
?	541	553	546	544	542	545	549	550	552	550	565	547	-
νU-O	522	526	526	523	522	523	522	524	525	523	521	522	525
?	443	434	422	455	476	489	467	475	465	469	-	-	-
νU-O + $\nu C\text{-}CH_3$	411	405	404	405	405	404	404	405	407	410	402	404	409
?	365	-	-	373	347	335	333	333	337	337	395	390	-
δO=U=O	273	272	269	258	272	271	272	275	278	272	274	273	272

Fig. 11.

Infrared Spectrum of $UO_2(ACA)_2$·acetylacetone ethylimine



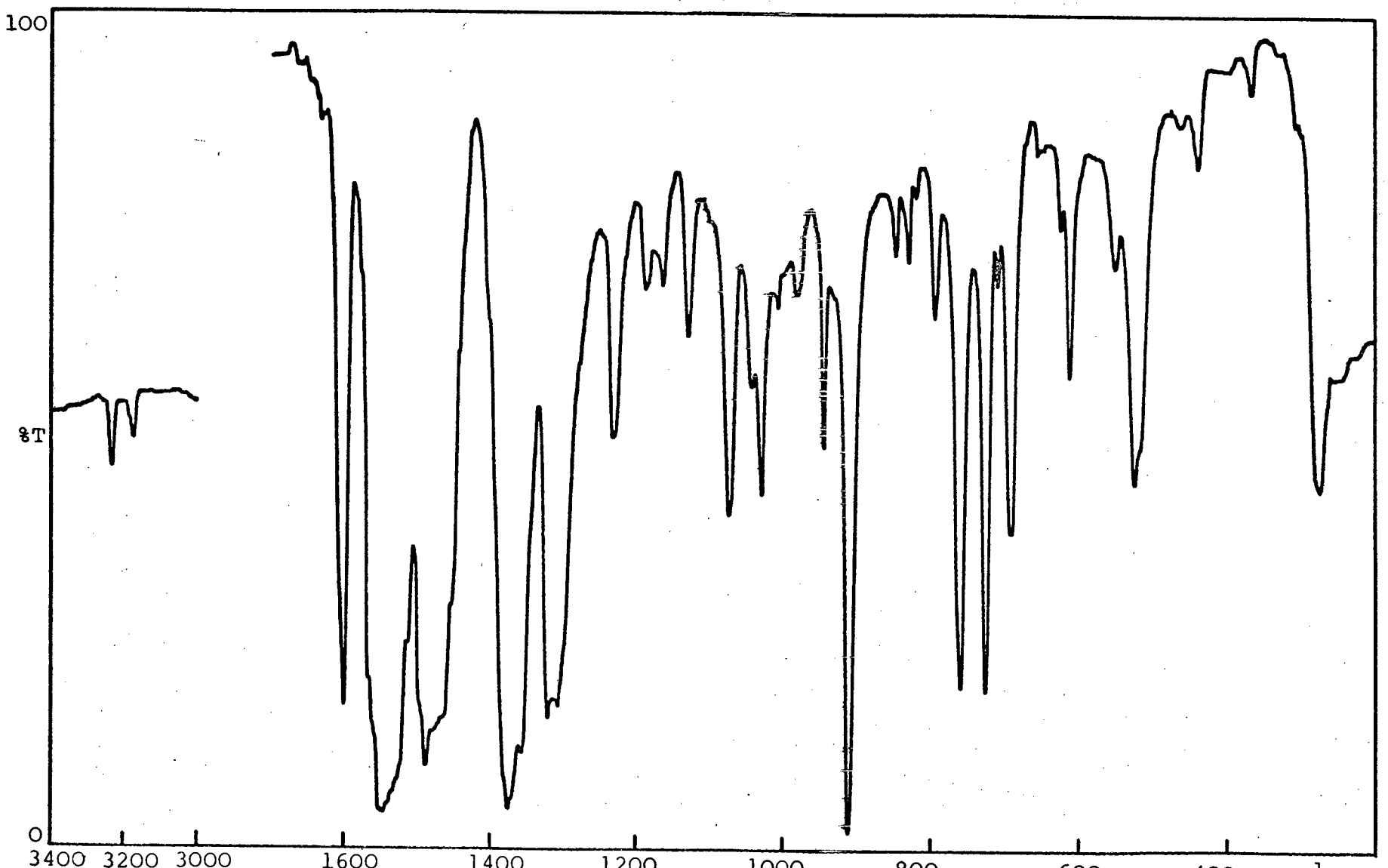
k. Primary Aliphatic Amine Adducts of Uranyl Dibenzoylmethanate

$UO_2(DBM)_2 \cdot RNH_2$

σ* x 10^3 and R	+600 C_6H_5	+490 H	+215 Bz	+80 β-PhEt	0 Me	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-150 Cx	-190 i-Pr	-210 s-Bu	-300 t-Bu
Assignment													
νN-H asym.	3328	3335	3338	3322	3341	3340	3345	3352	3341	3314	3332	3332	-
νN-H sym.	3262	3260	3283	3267	3281	3280	3282	3289	3278	3267	3272	3276	3269
Phenyl	1595	1595	1595	1594	1595	1594	1594	1594	1594	1595	1594	1594	1594
νC=O	1540	1542	1536	1541	1538	1532	1542	1540	1540	1540	1539	1543	1533
νC=C	1523	1523	1528	1525	1520	-	1524	1527	1524	-	1525	1527	1529
νC=C +	1319	1319	1316	1316	1315	1316	1316	1316	1316	1315	1317	1316	1315
νC-C_6H_5	1294	1299	1305	1304	1304	1301	1302	1302	1303	1306	1302	1303	1306
δC-H i.p.	1228	1215	1228	1225	1229	1228	1229	1226	1226	1230	1230	1227	1228
νU=O asym.	898	904	901	901	902	906	907	907	908	908	908	907	909
δC-H o.o.p.	804	812	813	811	815	-	817	817	-	816	817	-	-
	780	790	788	785	789	788	788	789	788	788	790	790	786
	753	754	749	751	761	759	757	755	756	752	755	755	756
Substitution	717	717	714	721	724	723	722	720	723	716	722	722	713
Patterns	683	687	684	687	687	688	688	688	687	685	686	688	685
	606	606	607	608	607	608	607	607	607	607	608	608	606
νU-N	516	535	525	533	539	539	540	544	539	-	555	547	559
νU-O	527	523	525	524	524	523	521	522	522	521	519	519	518
νU-O + νC-Ph	451	454	455	454	450	452	454	457	453	454	454	456	458
δO-U-O	430	427	434	430	430	435	434	433	433	434	434	434	435
δO=U=O	270	269	271	272	271	272	271	272	271	273	272	270	271

Fig. 12.

Infrared Spectrum of $UO_2(DBM)_2 \cdot s\text{-}C_4H_9NH_2$



1. Primary Aliphatic Amine Adducts of Uranyl

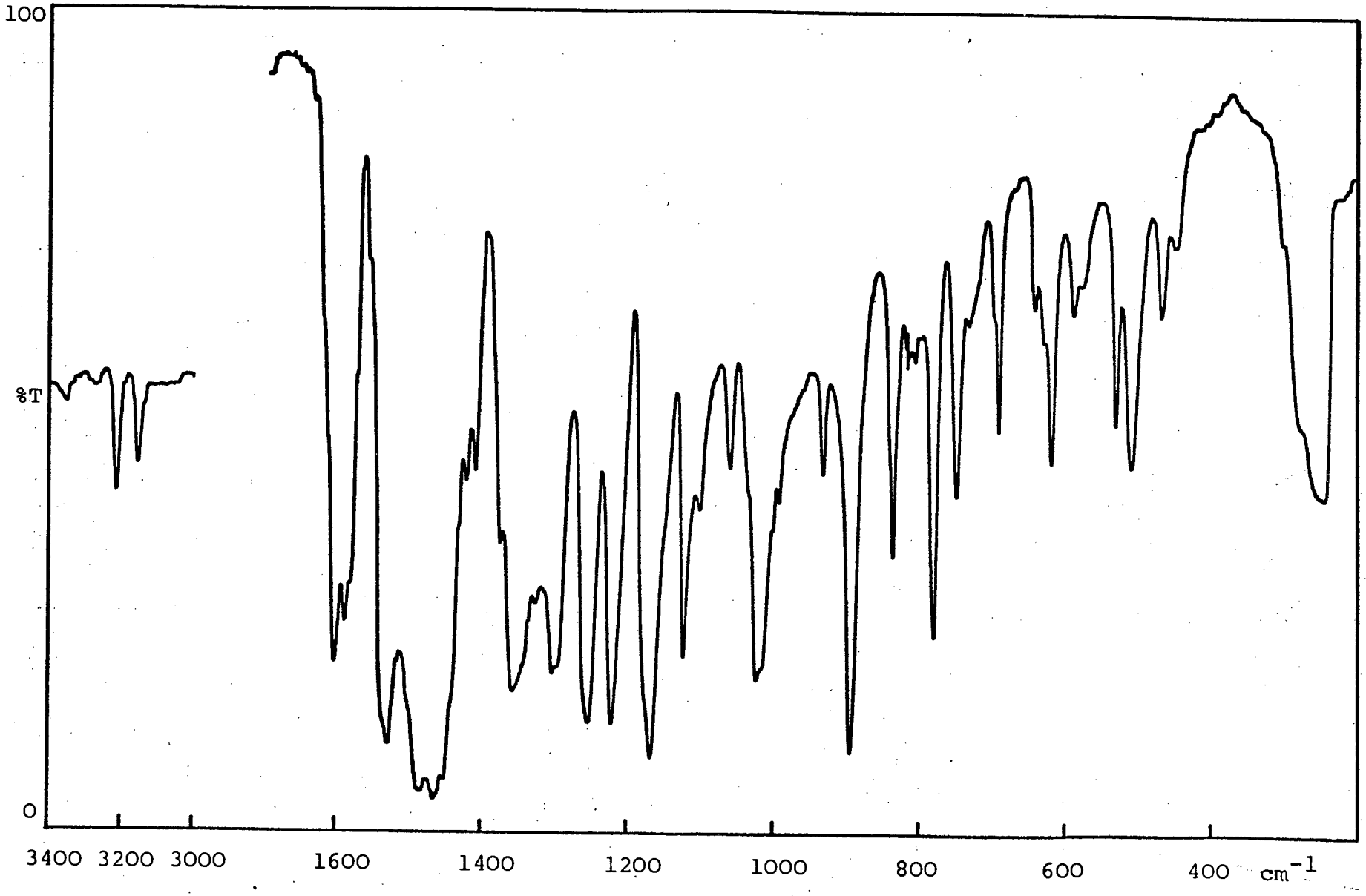
p, p' - Dimethoxydibenzoylmethanate

$UO_2(p\text{-MeODBM})_2 \cdot RNH_2$

σ^* x 10^3 and R	+600 C_6H_5	0 Me	-300 t-Bu
Assignment			
νN-H asym	3322	-	3356
νN-H sym.	3258	3284	-
Phenyl ?	1609	1609	1610
Phenyl	1596	1592	1597
νC=O	1537	1537	1536
νC=C	1493	1492	1499
νC=C + νC-Ph	1307	1301	1302
C-O-C	1262	1266	1266
δC-H i.p.	1230	1230	1231
νU=O asym.	892	896	902
δC-H o.o.p.	788	785	792
Substitution Patterns	756	738	733
	696	706	708
	624	624	625
?	594	586	588
?	580	-	576
?	536	537	541
?	518	-	-
?	509	513	519
νU-O + νC-Ph	470	472	468
δO-U-O	450	450	451
δO=U=O	279	280	282

Fig. 13.

Infrared Spectrum of $UO_2(p\text{-MeODBM})_2 \cdot$aniline



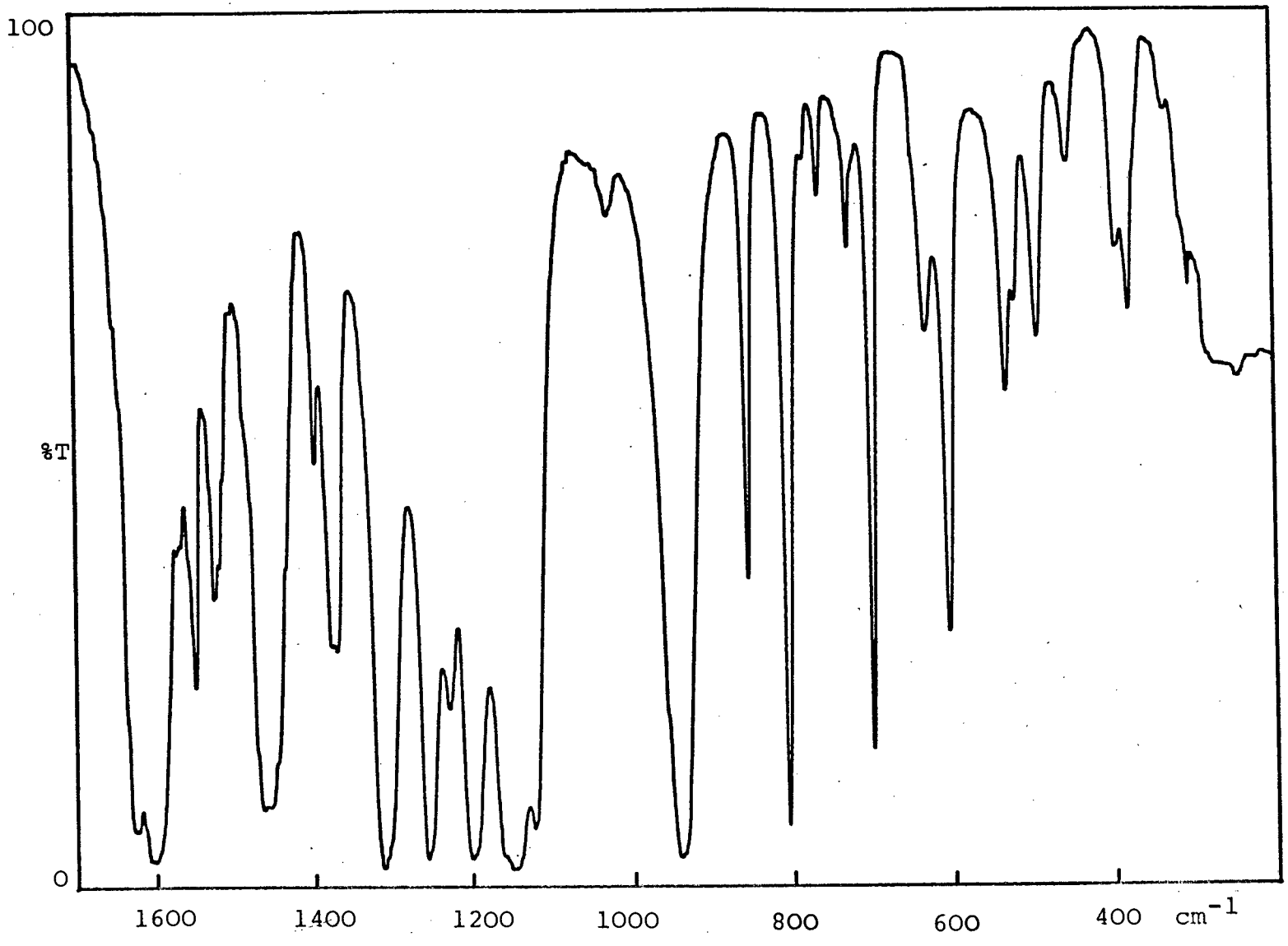
m. Vanadyl β-Ketoenolates

$VO(L)_2$

L	DPM	ACA	PTA	TFA	BZA	DBM	pMeO DBM
Assignment							
νC=O	1552	1564	1604	1616	1562	1544	1531
νC=C	1508	1536	1530	1540	1526	1531	1507
νC=C + νC-R	1302	1289	1316	1301	1313	1322	1310
δC-H i.p.	1202	1190	1149	1141	1210	1231	1236
CH_3 rock	1030	1022	-	1022	1031	-	1029
νV=O	1006	999	945	931	998	996	991
νC=O + νC-R	936	939	945	950	965	945	941
νC-CF_3	-	-	858	869	-	-	-
δC-H o.o.p.	803	800	807	806	855	817	794
Ring def.	741	689	702	736	-	-	-
	648	661	636	629	629	649	652
νV-O	-	611	607	602	575	589	562
?	524	-	498	-	-	-	-
νV-O + νC-R	490	488	456	449	462	467	485
δO-V-O	439	426	396	401	-	-	-
νV-O	377	367	331	323	381	374	375

Fig. 14.

Infrared Spectrum of $VO(PTA)_2$



n. Substituted Pyridine Adducts of Vanadyl Acetylacetonate

$VO(ACA)_2 \cdot R\text{-}C_5H_4N$

R	νC=O	νC=C	δC=C + $\nu C\text{-}CH_3$	δC-H i.p.	CH_3 rock	νV=O	νC=O + $\nu C\text{-}CH_3$	δC-H o.o.p.		Ring def.		νV-O		νV-O + $\nu C\text{-}CH_3$		δ O-V-O	νV-O	
$-CO_2C_2H_5$	1590	1538	1281	1200	1030	955	935	809	776	681	662	591	554	456	436	416	363	333
$-COC_6H_5$	1586	1534	1279	1199	1029	957	938	803	759	680	651	589	554	453	437	414	358	337
$-C_6H_5$	1590	1535	1280	1196	1024	955	933	796	776	683	664	591	551	460	431	418	348	332
,5-di-CH_3	1597	1532	1273	1194	1025	959	935	797	774	679	665	588	550	458	431	410	347	-
$-C_2H_5$	1586	1537	1273	1202	1028	959	932	818	789	681	660	589	553	452	434	414	361	338
$-NH_2$	1586	1529	1275	1200	1025	959	937	809	789	682	656	592	551	459	435	417	349	-
$-t\text{-}C_4H_9$	1595	1535	1276	1200	1027	962	931	798	792	679	662	589	550	450	436	416	345	-
$-N(CH_3)_2$	1595	1539	1280	1195	1022	953	930	790	781	681	665	589	555	455	434	406	348	336
$-NH_2$	1572	1539	1283	1200	1027	958	939	800	792	684	661	593	551	458	438	418	349	338
-CN	1590	1539	1284	1196	1027	974	934	793	-	687	661	603	-	466	-	418	363	-
	1586	1540	1282	1201	1028	973	941	784	-	683	660	601	-	465	-	422	362	-
$-n\text{-}C_3H_7$	1588	1532	1283	1198	1029	971	939	793	-	682	662	606	-	465	-	423	363	-
$-CH_3$	1575	1533	1285	1198	1030	971	943	797	-	682	664	605	-	465	-	421	363	-
,4-di-CH_3	1570	1525	1279	1199	1020	965	934	794	-	677	661	602	-	462	-	421	363	-

Fig. 15.

Infrared spectrum of $VO(ACA)_2 \cdot 4\text{-}CH_3C_5H_4N$

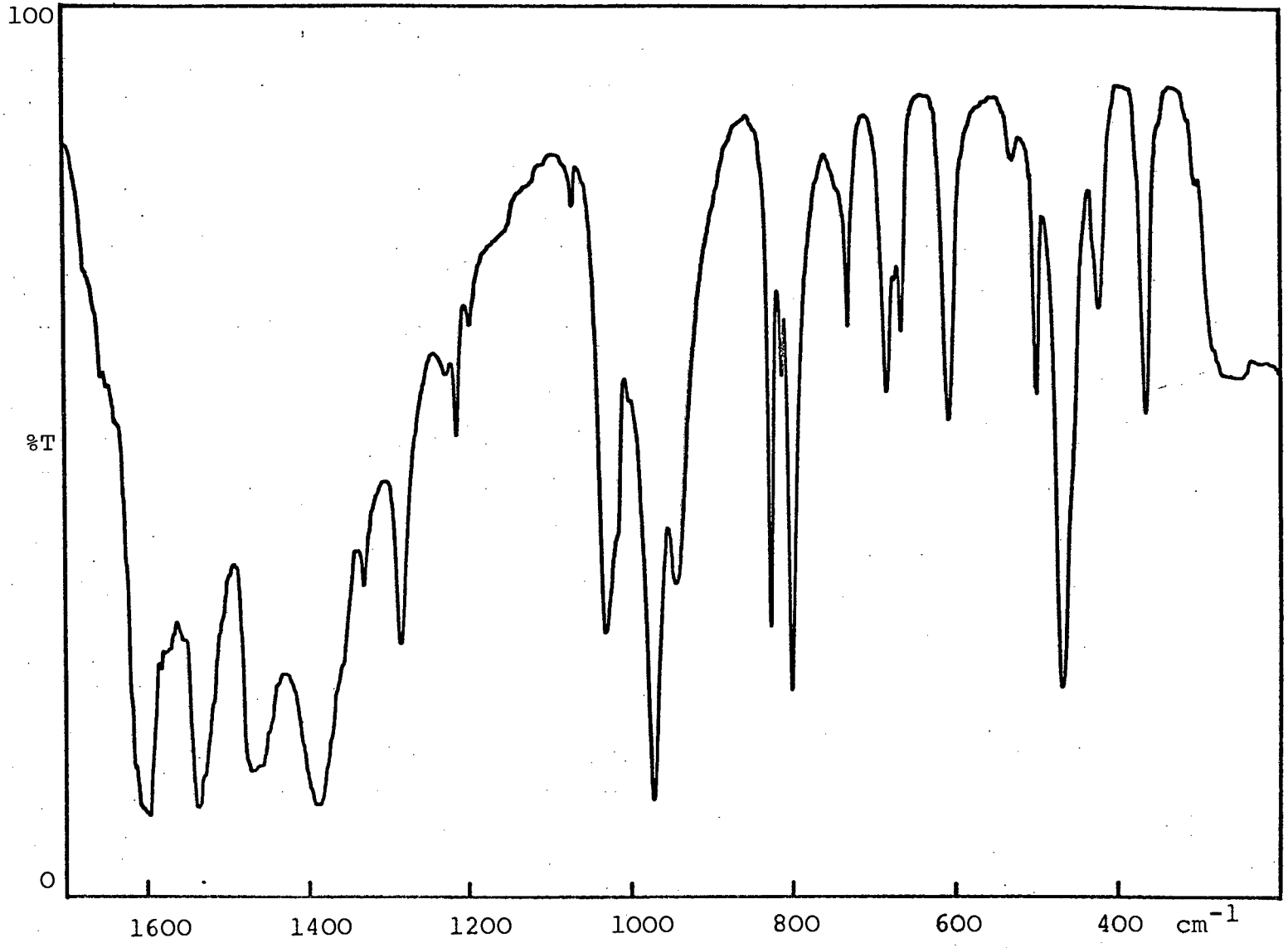
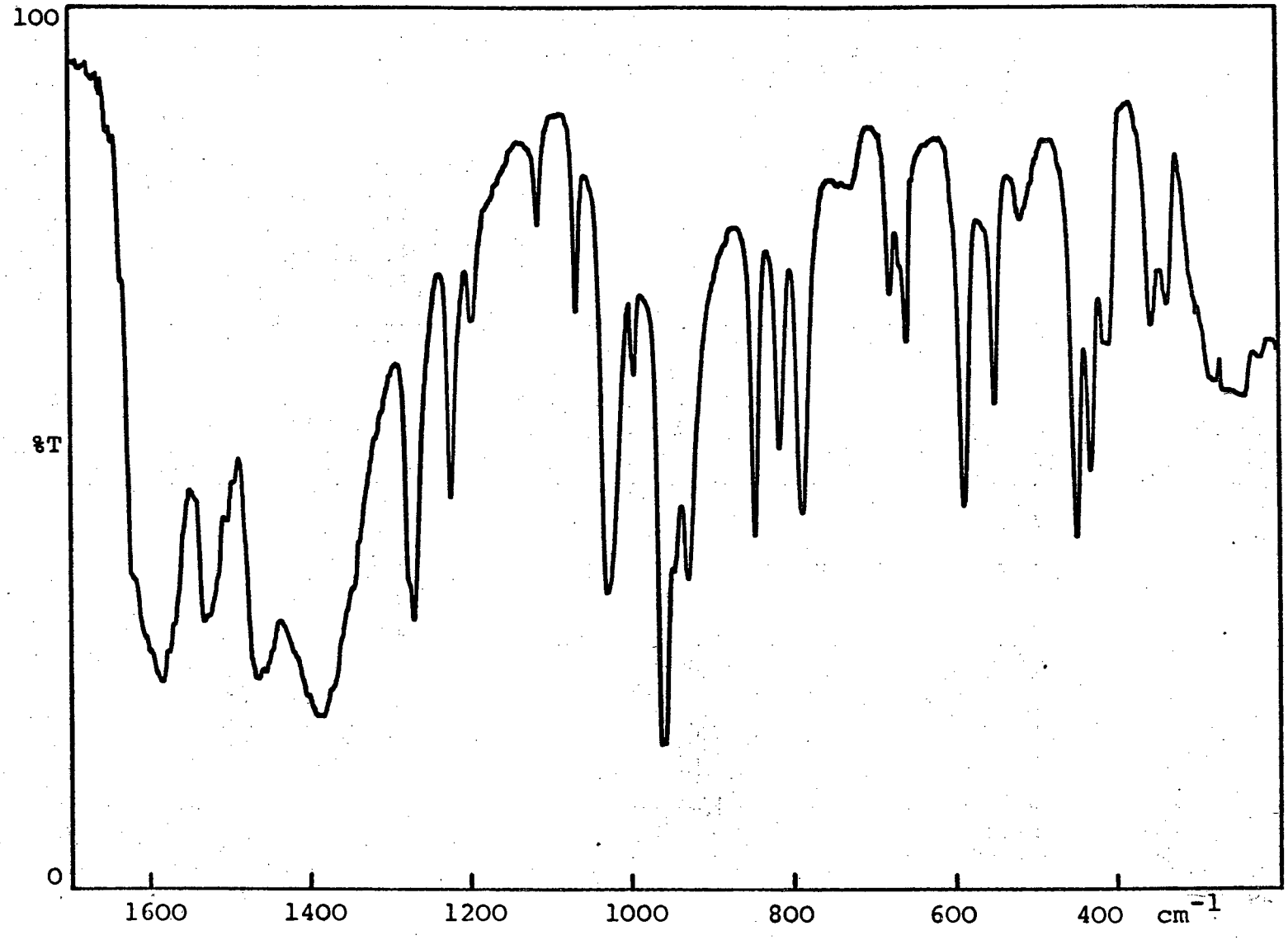


Fig. 16.

Infrared Spectrum of $VO(ACA)_2 \cdot 4\text{-}C_2H_5C_5H_4N$



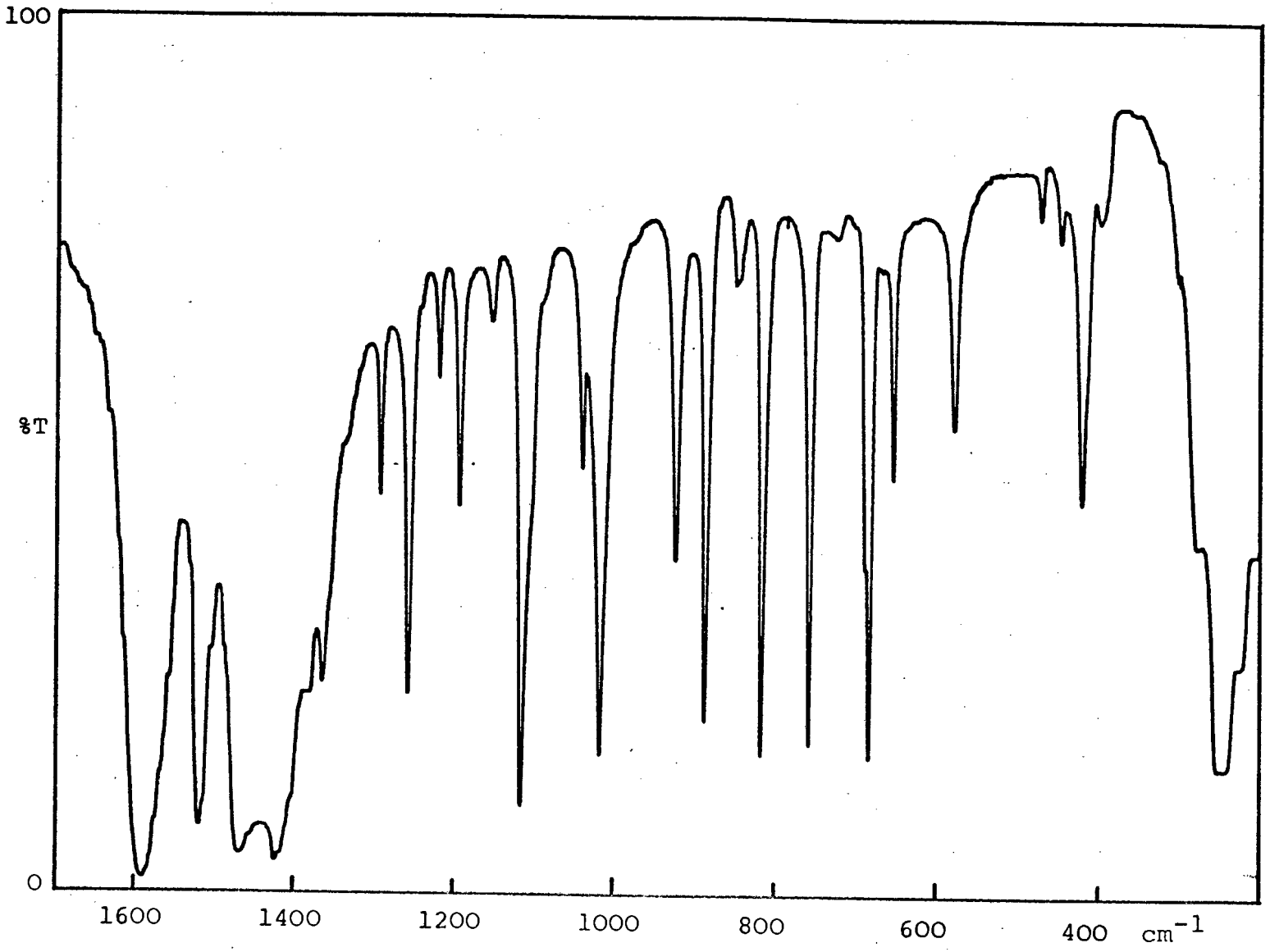
o. Substituted Pyridine Adducts of Nickel Acetylacetonate

$Ni(ACA)_2 \cdot R\text{-}C_5H_4N$

R	σ x 10^2	νC=O	νC=C	δC=C + νC-CH_3	δC-H i.p.	CH_3 rock	νC=O + νC-CH_3	δC-H o.o.p.		Ring def.	νNi-O	νNi-O + νC-CH_3
3,5-di-Cl	+75	1590	1528	1260	1197	1020	927	821	760	658	585	425
3-CN	+68	1591	1525	1260	1198	1016	927	814	762	651	584	424
4-CN	+63	1592	1524	1261	1199	1019	927	839	776	664	584	424
4-CO_2CH_3	-	1594	1520	1265	1200	1021	929	831	775	660	583	423
4-$CO_2C_2H_5$	+52	1593	1521	1263	1201	1021	927	-	770	660	583	423
4-$COCH_3$	+52	1594	1524	1267	1197	1022	926	830	770	661	583	423
4-COC_6H_5	+46	1594	1525	1264	1197	1020	925	795	776	665	582	423
3-$CO_2C_2H_5$	+40	1597	1525	1264	1192	1024	928	-	769	660	582	422
3-Br	+39	1596	1527	1262	1199	1020	927	799	766	657	583	422
3-I	+35	1596	1526	1261	1201	1019	927	796	770	656	582	423
3-CO_2CH_3	+32	1597	1524	1263	1197	1020	927	833	770	660	581	422
3-COC_6H_5	-	1598	1519	1259	1196	1020	924	790	766	658	580	423
3-$COCH_3$	+31	1597	1519	1260	1198	1022	923	815	777	650	581	421
4-C_6H_5	+ 1	1602	1519	1259	1195	1019	920	-	767	659	579	419
H	0	1602	1526	1259	1202	1015	923	-	769	656	578	419
3-C_2H_5	- 4	1602	1526	1257	1201	1018	926	812	765	660	578	419
4-$CH_2C_6H_5$	-	1603	1518	1259	1194	1014	924	-	764	656	579	419
4-n-C_3H_7	-13	1603	1524	1260	1197	1020	926	808	761	657	577	418
3,5-di-CH_3	-14	1604	1521	1257	1198	1015	922	-	760	656	577	418
4-C_2H_5	-15	1604	1524	1259	1197	1019	924	-	760	657	577	418
4-CH_3	-17	1604	1526	1255	1202	1025	925	813	764	657	577	418
4-t-C_4H_9	-20	1606	1519	1257	1198	1019	924	833	762	656	576	417
3,4-diCH_3	-24	1606	1521	1260	1200	1016	924	825	761	657	576	417
4-$N(CH_3)_2$	-60	1612	1531	1255	1195	1016	921	805	758	656	572	413

Fig. 17.

Infrared Spectrum of $Ni(ACA)_2 \cdot 3,5\text{-di-}ClC_5H_3N$



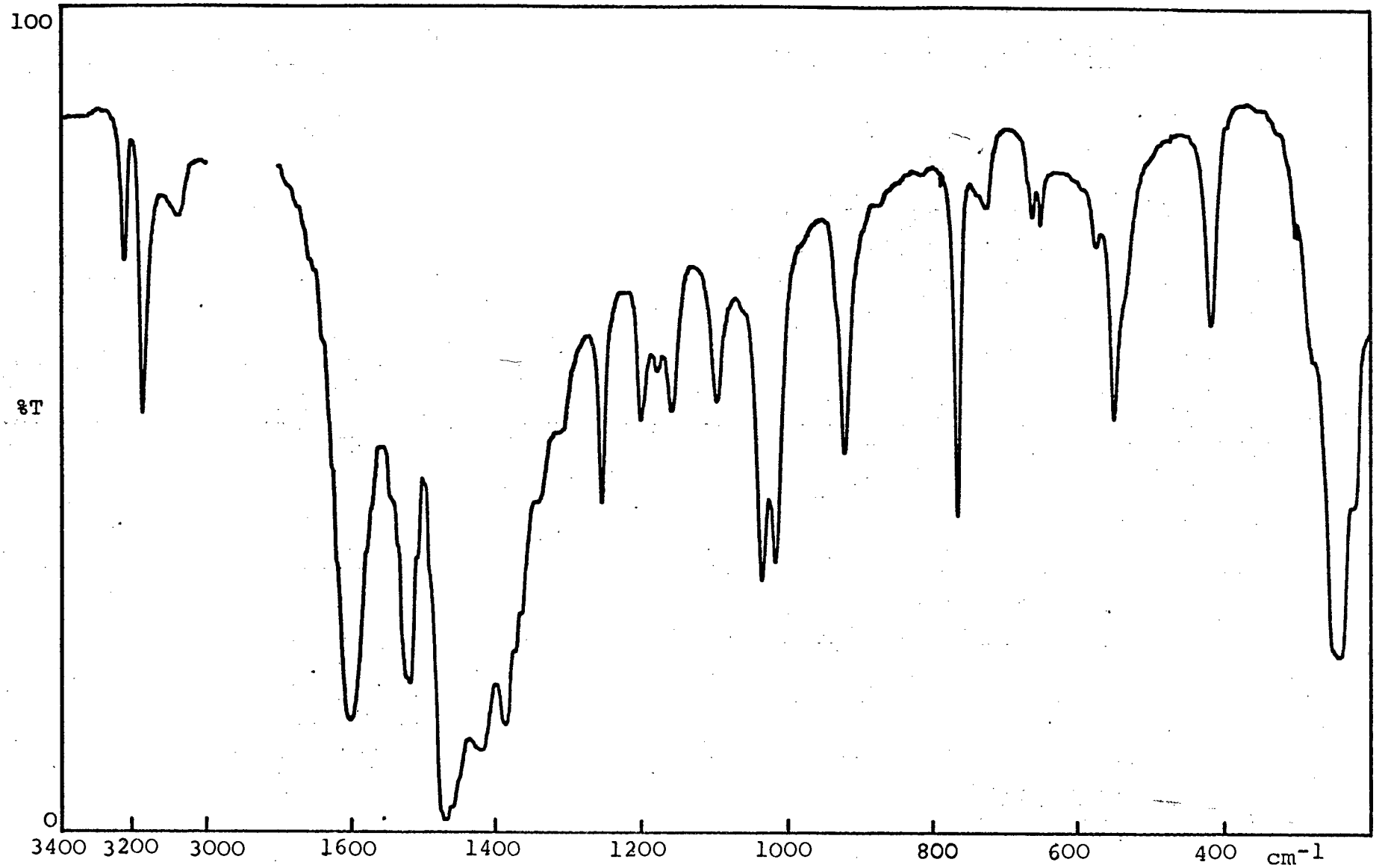
p. Primary Aliphatic Amine Adducts of Cobalt Acetylacetonate

$Co(ACA)_2 \cdot RNH_2$

σ^* x 10^3 and R	+600 C_6H_5	+490 H	+215 Bz	+80 β-PhEt	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-190 i-Pr	-210 s-Bu
Assignment										
νN-H asym	3325	3355	3322	3321	3322	3325	3335	3320	3319	3323
νN-H sym.	3280	3282	3280	3282	3286	3282	3286	3282	3282	3280
νC=O + δN-H	1604	1620	1593	1602	1606	1603	1600	1604	1603	1597
νC=C	1517	1526	1516	1518	1516	1519	1523	1517	1520	1518
δC=C + $\nu C-CH_3$	1261	1256	1256	1253	1253	1252	1254	1252	1254	1254
δC-H i.p.	1198	1203	1196	1197	1193	1196	1201	1196	1200	1196
CH_3 rock	1022	1017	1012	1016	1016	1014	1016	1014	1015	1015
νC=O + $\nu C-CH_3$	928	927	925	920	920	922	923	921	923	922
δC-H o.o.p.	765	765	766	-	763	767	768	764	764	763
Ring def.	662	661	650	652	656	652	651	650	658	658
νCo-O	561	559	554	553	553	553	551	551	553	552
νCo-O + $\nu C-CH_3$	421	416	414	414	413	414	414	413	412	412

Fig. 18.

Infrared Spectrum of $Co(ACA)_2 \cdot i\text{-}C_4H_9NH_2$



3. NUCLEAR MAGNETIC RESONANCE RESULTS

All shifts are p.p.m. downfield of TMS.

a. 3- and 4- Substituted Pyridines

$R\text{-}C_5H_4N$

R	H_2	H_3	H_4	H_5	H_6
4-CN	8.82	7.54	-	7.54	8.82
4-CHO	8.88	7.70	-	7.70	8.88
$4\text{-}COC_6H_5$	8.79	7.55	-	7.55	8.79
$4\text{-}COCH_3$	8.77	7.72	-	7.72	8.77
$4\text{-}CO_2C_2H_5$	8.75	7.80	-	7.80	8.75
$4\text{-}CO_2CH_3$	8.74	7.79	-	7.79	8.74
$4\text{-}C_6H_5$	8.62	7.44	-	7.44	8.62
$4\text{-}t\text{-}C_4H_9$	8.48	7.21	-	7.21	8.48
$4\text{-}n\text{-}C_3H_7$	8.47	7.08	-	7.08	8.47
$4\text{-}C_2H_5$	8.47	7.09	-	7.09	8.47
$4\text{-}CH_2C_6H_5$	8.45	7.05	-	7.05	8.45
$4\text{-}(CH_2)_3OH$	8.42	7.13	-	7.13	8.42
$4\text{-}CH_3$	8.40	7.04	-	7.04	8.40
$4\text{-}CH_2OH$	8.39	7.30	-	7.30	8.39
$4\text{-}N(CH_3)_2$	8.18	6.45	-	6.45	8.18
$4\text{-}NH_2$	8.18	6.50	-	6.50	8.18
$3\text{-}CO_2C_2H_5$	9.20	-	8.29	7.35	8.74
$3\text{-}CO_2CH_3$	9.20	-	8.27	7.37	8.76
$3\text{-}COCH_3$	9.18	-	8.25	7.44	8.79
$3\text{-}COC_6H_5$	8.98	-	8.12	7.42	8.79
3-CN	8.86	-	7.99	7.43	8.82
3-I	8.85	-	8.25	7.07	8.55
3-Br	8.65	-	7.77	7.13	8.48
3-Cl	8.59	-	7.66	7.21	8.49
$3\text{-}CH_2OH$	8.45	-	7.70	7.24	8.38
$3\text{-}C_2H_5$	8.43	-	7.52	7.18	8.43
$3\text{-}CH_3$	8.43	-	7.48	7.15	8.40
3-OH	8.26	-	7.48	7.45	8.07
$3\text{-}NH_2$	8.02	-	7.00	6.94	7.91

b. 2- and Di-substituted Pyridines

R	H_2	H_3	H_4	H_5	H_6
2-Br	-	7.31	7.59	7.31	8.35
2-Cl	-	7.14	7.65	7.14	8.37
$2\text{-}CH_2CH_2OH$	-	7.11	7.61	7.22	8.45
$2\text{-}(CH_2)_3OH$	-	7.10	7.59	7.22	8.45
$2\text{-}CH_3$	-	7.05	7.55	7.17	8.49
$2\text{-}NH_2$	-	6.44	7.37	6.64	8.04
$2\text{-}NH_2$, $3\text{-}CH_3$	-	-	7.22	6.55	7.92
$2,4\text{-di-}CH_3$	-	6.93	-	7.36	8.21
$2\text{-}NH_2,4\text{-}CH_3$	-	6.27	-	6.44	7.91
$3\text{-}C_2H_5,4\text{-}CH_3$	8.45	-	-	7.05	8.27
$3,4\text{-di-}CH_3$	8.26	-	-	6.99	8.26
$2\text{-}NH_2,6\text{-}CH_3$	-	6.25	7.27	6.42	-
H	Complex	Complex	Complex	7.22	8.60

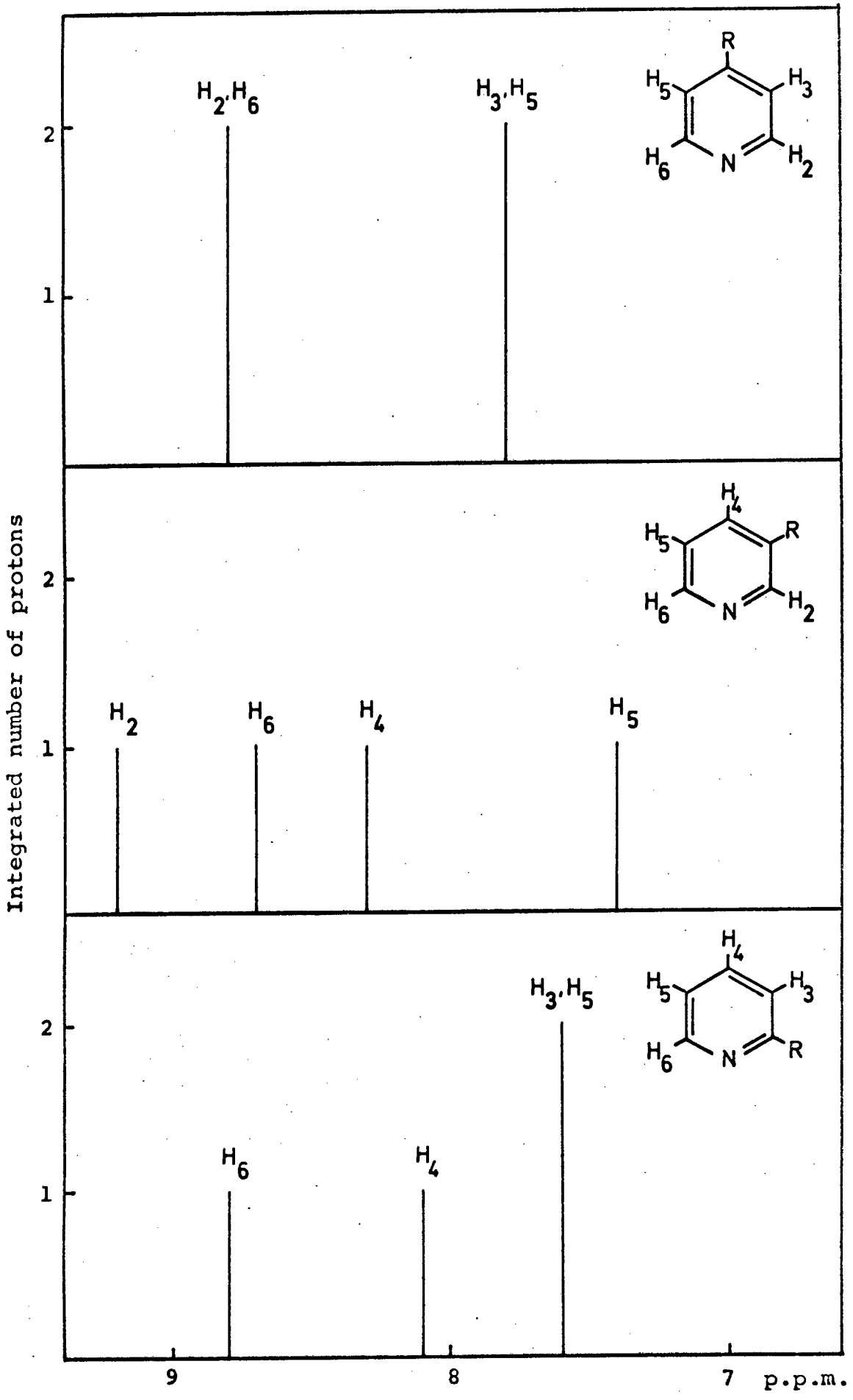


Fig. 19.

Typical stylized NMR spectra of

c. Substituted Pyridine Adducts of Uranyl Acetylacetonate

$UO_2(ACA)_2 \cdot R\text{-}C_5H_4N$

R	H_2	H_3	H_4	H_5	H_6	C-H of ACA ring	CH_3 of ACA ring
4-CN	9.55	7.83	-	7.83	9.55	5.87	2.37
4-$COCH_3$	9.66	8.04	-	8.04	9.66	5.82	2.37
4-$CO_2C_2H_5$	9.67	8.21	-	8.21	9.67	5.82	2.33
4-CO_2CH_3	9.07	7.99	-	7.99	9.07	5.62	2.15
4-C_6H_5	9.51	7.85	-	7.85	9.51	5.86	2.37
4-t-C_4H_9	9.51	7.65	-	7.65	9.51	5.82	2.35
4-n-C_3H_7	9.45	7.47	-	7.47	9.45	5.82	2.35
4-C_2H_5	9.45	7.47	-	7.47	9.45	5.82	2.33
4-CH_3	9.42	7.50	-	7.50	9.42	5.83	2.35
3-CH_3	9.35	-	7.83	7.55	9.28	5.82	2.33
3,4-di-CH_3	9.28	-	-	7.43	9.28	5.82	2.34
H	9.57	7.73	7.96	7.73	9.57	5.85	2.35

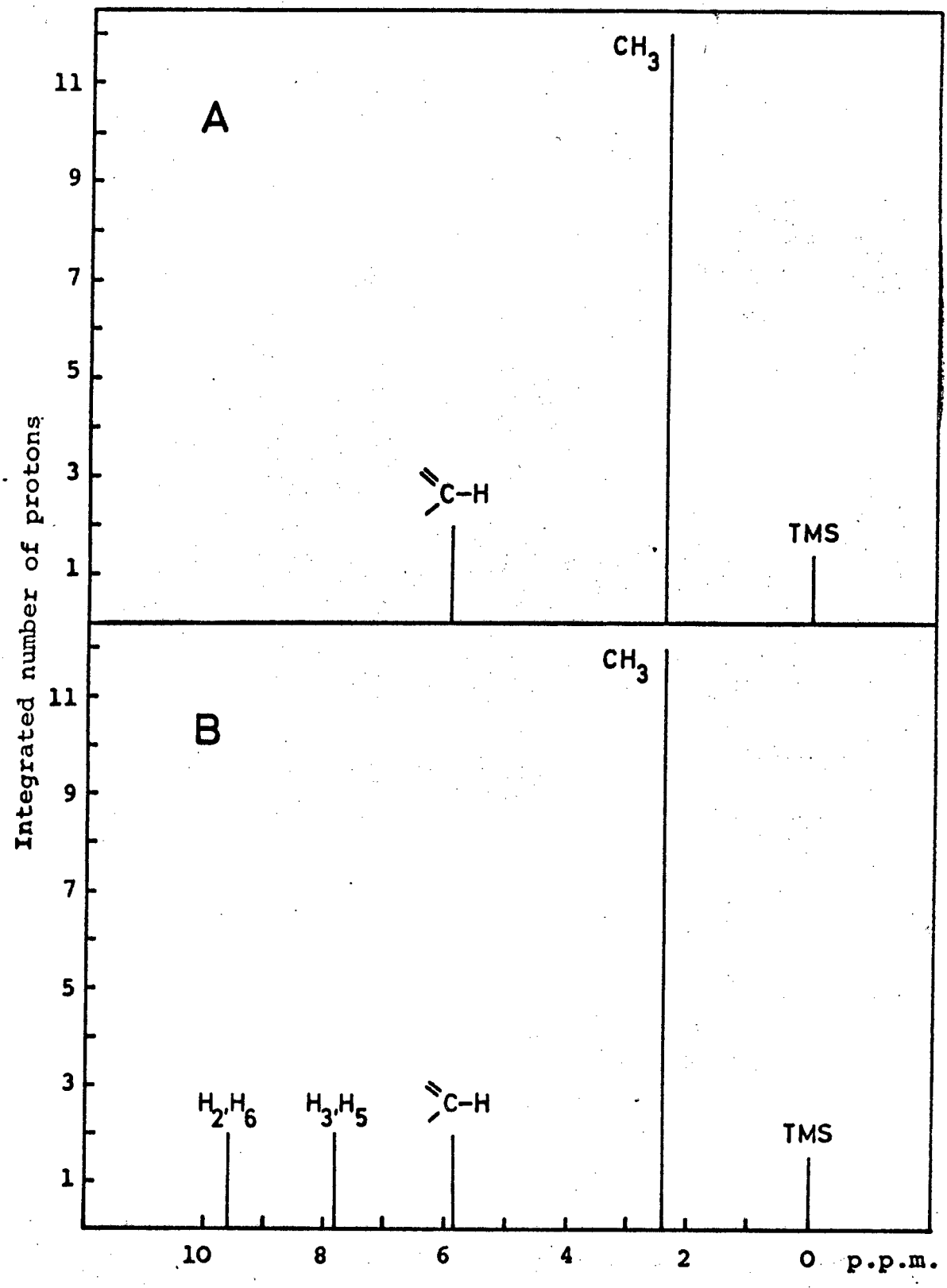


Fig. 20.

Stylized NMR spectra of:

A; $UO_2(ACA)_2$, B; $UO_2(ACA)_2 \cdot 4\text{-}CNC_5H_4N$

d. Pyridine Adducts of Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot py$

L	H_2	H_3	H_4	H_5	H_6	C-H of ring	CH_3 of ring
TFA	9.20	7.75	8.12	7.75	9.20	6.28	2.60
DPM	9.36	7.73	8.00	7.73	9.36	6.11	-
PVA	9.46	7.73	7.98	7.73	9.46	5.96	2.38
EAA	9.47	7.72	7.98	7.72	9.47	5.31	2.28
ACA	9.57	7.73	7.96	7.73	9.57	5.85	2.35
DBM	9.63	7.73	7.88	7.73	9.63	7.24	-
MAC	9.59	7.73	7.95	7.73	9.59	-	2.44

e. Pyridine N-Oxide Adducts of Uranyl β-Ketoenolates

$UO_2(L)_2 \cdot pyNO$

L	H_2	H_3	H_4	H_5	H_6	C-H of ring	CH_3 of ring
DPM	9.13	7.56	7.46	7.56	9.13	6.10	-
TFA	9.09	7.70	7.63	7.70	9.09	6.24	2.56
BZA	9.03	7.57	7.53	7.57	9.03	6.50	2.47
DBM	9.03	7.57	7.52	7.57	9.03	7.18	-
ACA	8.95	7.61	7.55	7.61	8.95	5.78	2.30

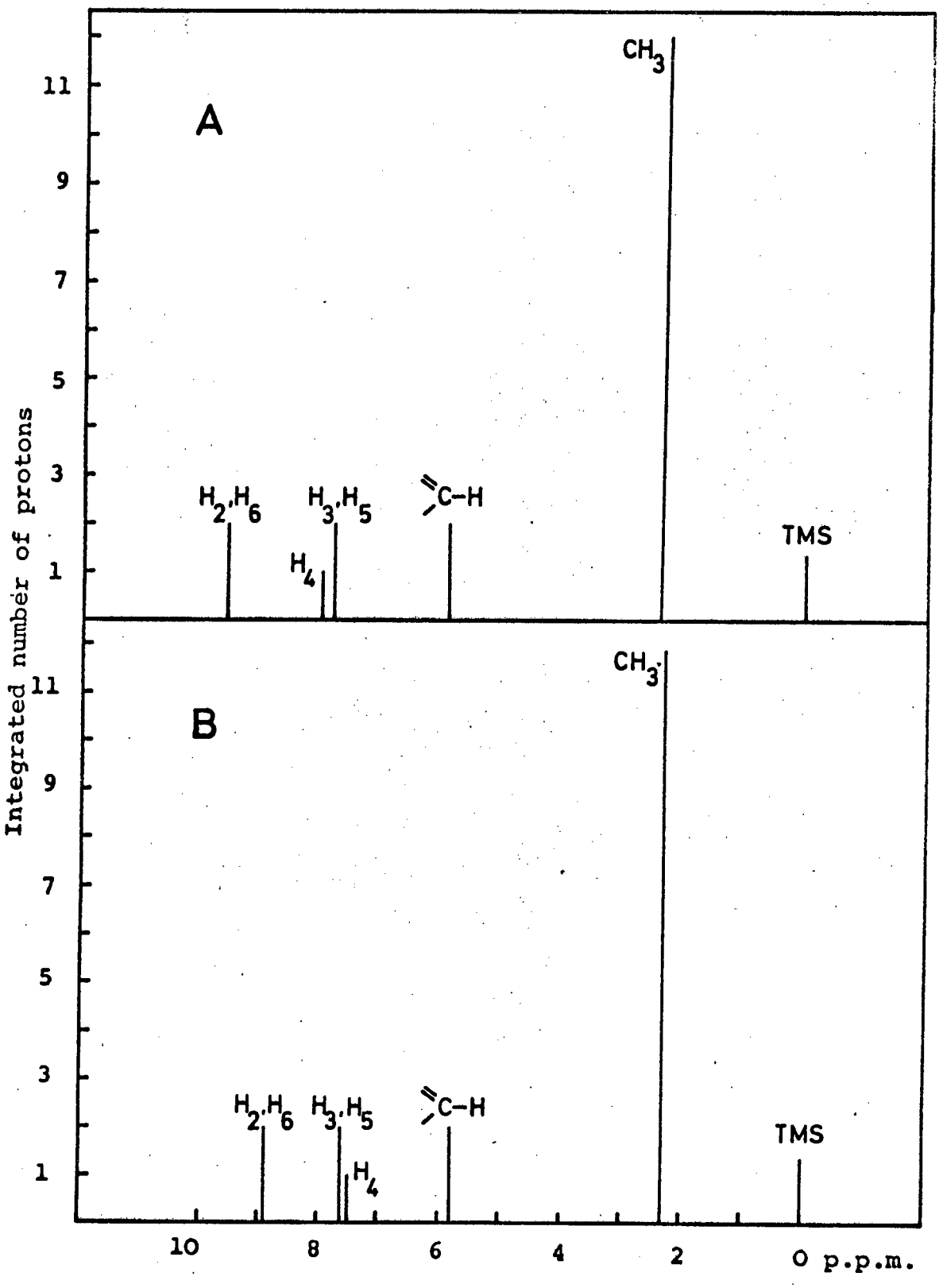


Fig. 21.

Stylized NMR spectra of:

A; $UO_2(ACA)_2 \cdot C_5H_5N$, B; $UO_2(ACA)_2 \cdot C_5H_5NO$

f. β-Ketoimines

$H_3C-CO-CH=C(CH_3)-NHR$

σ* x 10^3 and R	+600 C_6H_5	+490 H	+215 Bz	+80 β-PhEt	0 Me	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-150 Cx	-190 i-Pr	-300 t-Bu	- di-Me	- di-Et
Assignment														
N-H····O	12.47	9.60	11.14	10.88	10.55	10.80	10.68	10.82	10.70	10.97	10.67	11.33	-	-
D_2O	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C-H	5.18	5.03	5.03	4.92	4.99	4.96	4.95	4.94	4.95	4.91	4.92	4.90	5.03	5.10
D_2O	5.17	5.02	5.02	4.92	4.98	4.95	4.95	4.94	4.94	4.90	4.92	4.90	5.03	5.10
$O=C-CH_3$	2.08	2.02	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.99	1.98	2.06	2.50	2.52
D_2O	2.08	2.02	1.98	1.98	1.97	1.98	1.98	1.98	1.98	1.99	1.96	2.06	2.50	2.52
$N-C-CH_3$	1.97	1.91	1.88	1.79	1.92	1.93	1.92	1.91	1.92	1.93	1.96	1.97	2.06	2.06
D_2O	1.97	1.90	1.88	1.78	1.91	1.93	1.92	1.90	1.91	1.93	1.94	1.97	2.06	2.06

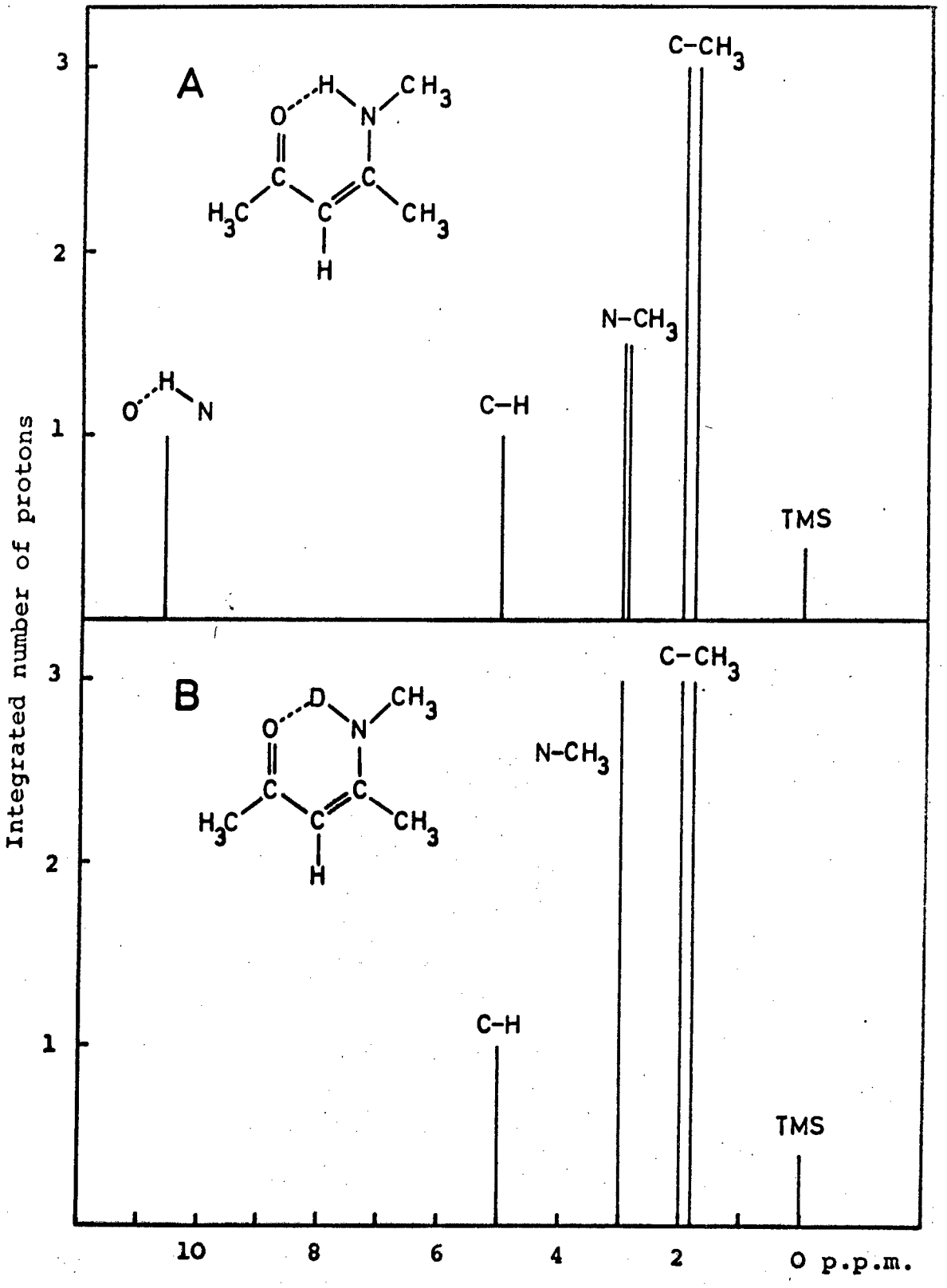


Fig. 22.

Stylized NMR spectra of:

A; Acetylacetone methylimine,

B; The same, deuterated.

g. β-Ketoimine Adducts of Uranyl Acetylacetonate

$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)\text{-}NHR$

σ* x 10^3 and R	+600 C_6H_5	+490 H	0 Me	-100 Et	-115 n-Pr	-125 i-Bu	-130 n-Bu	-190 i-Pr	-300 t-Bu	- di-Me	- di-Et
Assignment											
N-H···O	13.25	10.80	11.62	11.52	11.52	11.45	11.52	11.44	11.92	-	-
D_2O	-	-	-	-	-	-	-	-	-	-	-
C-H ACA	5.73	5.80	5.77	5.77	5.77	5.80	5.79	5.77	5.78	5.77	5.77
D_2O	5.74	5.80	5.78	5.78	5.79	5.82	5.78	5.78	5.78	5.75	5.78
C-H adduct	5.57	5.31	5.35	5.31	5.33	5.30	5.33	5.29	5.26	5.42	5.45
D_2O	5.50	5.27	5.31	5.30	5.29	-	5.28	5.23	-	5.38	5.44
$O{=}C\text{-}CH_3$ adduct	2.65	2.62	2.52	2.47	2.47	2.42	2.47	2.42	2.40	2.95	2.99
D_2O	2.55	2.53	2.47	2.40	2.42	2.37	2.40	2.35	2.33	2.90	2.98
CH_3 ACA	2.24	2.32	2.33	2.32	2.33	2.35	2.35	2.34	2.36	2.35	2.35
D_2O	2.24	2.33	2.35	2.30	2.35	2.37	2.35	2.35	2.36	2.30	2.35
$N\text{-}C\text{-}CH_3$ adduct	2.17	1.92	2.05	2.05	2.08	2.08	2.09	2.12	2.27	2.55	2.53
D_2O	2.15	1.93	2.05	2.07	2.08	2.07	2.08	2.10	2.27	2.48	2.53

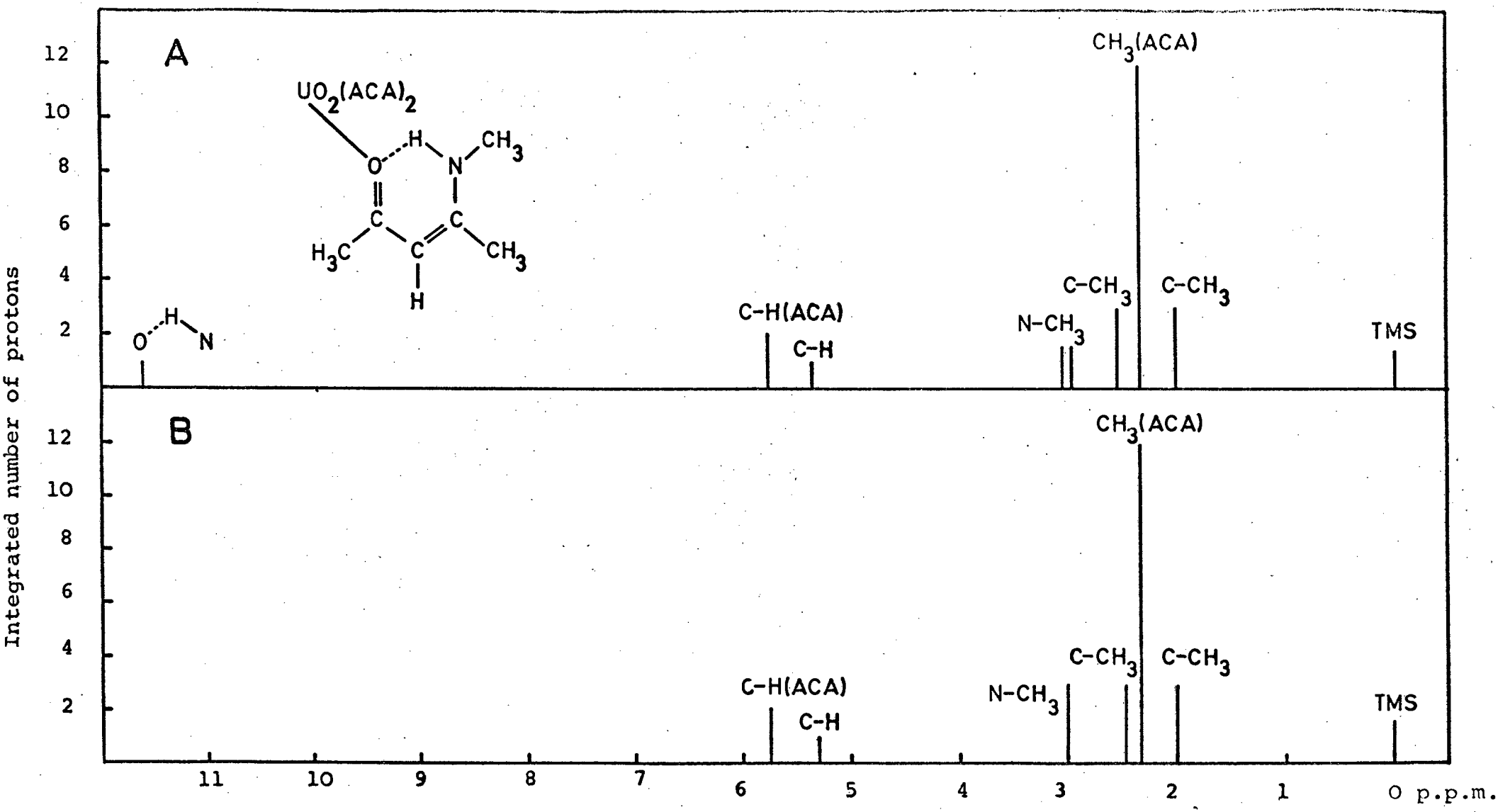


Fig. 23.

Stylized NMR spectra of A. $UO_2(ACA)_2$·acetylacetone methylimine.

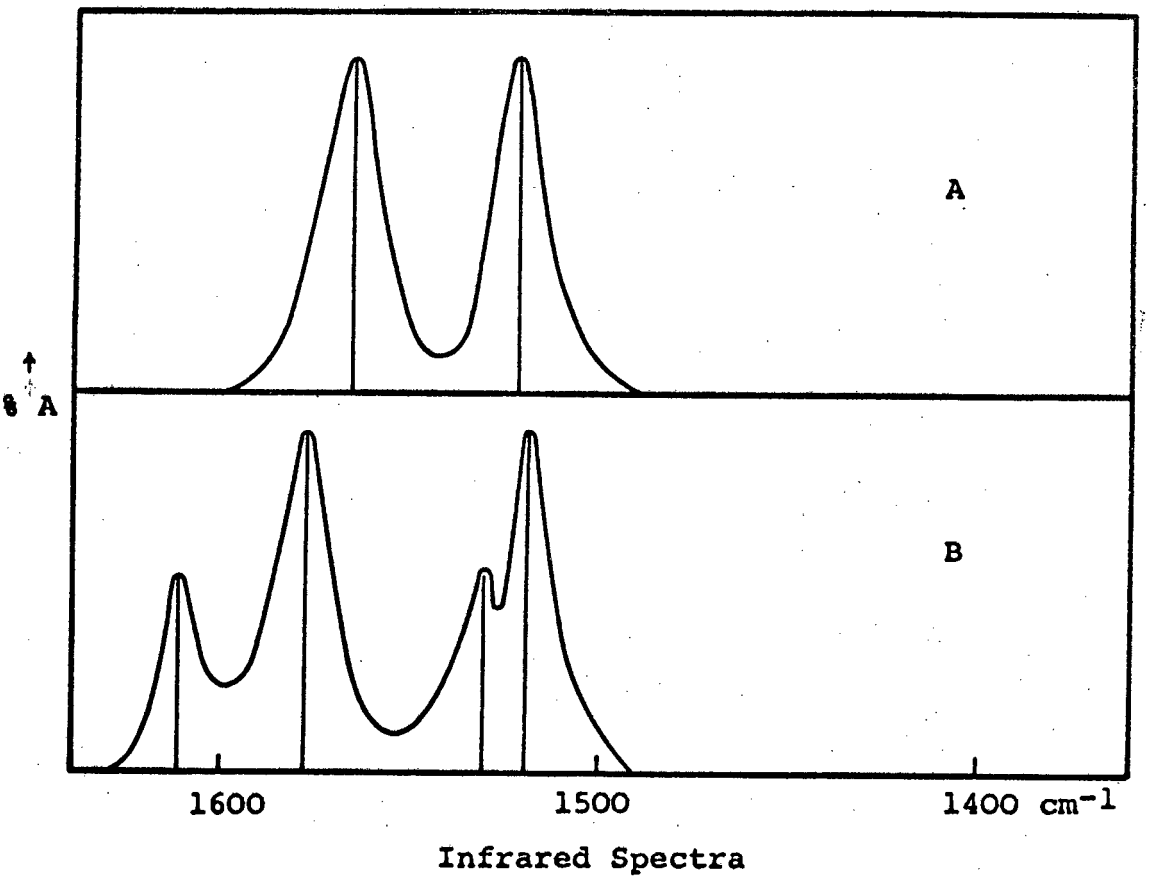
B. The same, deuterated

IV. DISCUSSION

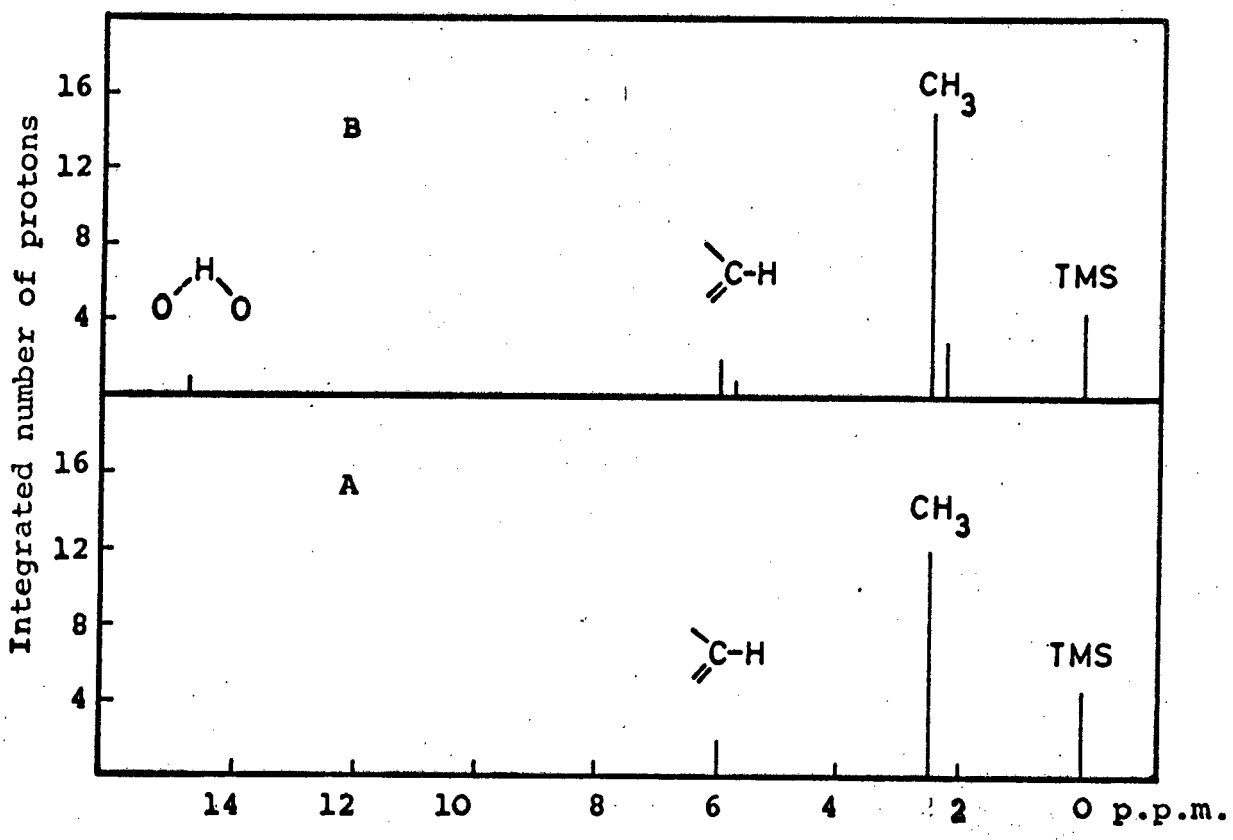
1. β-KETOIMINE ADDUCTS OF URANYL ACETYLACETONATE

The original intention of this portion of this work was the preparation of a series of primary aliphatic amine adducts of $UO_2(ACA)_2$. It was intended that the effect on the $UO_2(ACA)_2$ entity of a substituent exocyclic to the chelate ring would be studied. It was assumed that an aliphatic amine (or ammonia) would coordinate with the uranyl moiety in an analogous manner to pyridine,[43] *i.e.* by the formation of a bond between the uranium and nitrogen atoms. Although microanalytical results were consistent with amine adduct formation they also indicated the presence of an extra molecule of acetylacetone in the complex. The IR spectra indicate that the uranyl moiety is still present in the products, *i.e.* the oxidation number of uranium is apparently unaffected. It can thus be concluded that the extra acetylacetone molecule cannot be coordinated in the same way as the two "normal" acetylacetone molecules.

In an attempt to elucidate the molecular structures of these products, the acetylacetone adduct of uranyl acetylacetonate was studied. This complex was prepared by recrystallization of $UO_2(ACA)_2 \cdot H_2O$ from acetylacetone. The resultant orange crystals were filtered at the pump and air dried. (Found: C, 31·7; H, 3·9; U, 41·8%; calcd. for $C_{15}H_{22}O_8U$: C, 31·7; H, 3·9; U, 41·9%). The IR spectrum of this complex establishes the presence of the uranyl group. There are, therefore, two possible ways of formulating this complex:



Infrared Spectra



NMR Spectra

Fig. 24.

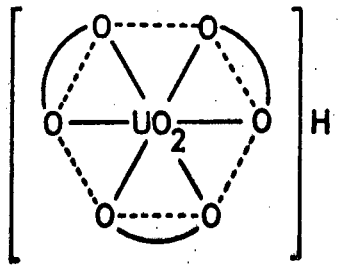
Comparison of IR and NMR spectra of:

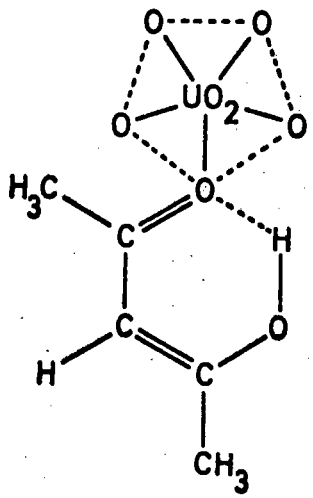
A: $UO_2(ACA)_2$, B: $UO_2(ACA)_2 \cdot HACA$

probably due to the CH_3 groups of the chelate rings. A combination of all the above evidence would seem to indicate that the correct formula for the acetylacetone adduct of $UO_2(ACA)_2$ is $UO_2(ACA)_2 \cdot HACA$.

It has been found from X-ray crystallographic studies[50,53-54] that various phosphine and arsine oxide complexes of both uranyl nitrate and uranyl acetate are 8-coordinate, *e.g.* $UO_2(NO_3)_2(R_3PO)_2$. Neutron diffraction[51] and X-ray studies[52] have shown that uranyl nitrate hexahydrate is also 8-coordinate, two of the water molecules being coordinated to the uranium atom, the other four being held in the crystal lattice by hydrogen bonding. There is a possibility, therefore, that $UO_2(ACA)_2 \cdot HACA$ may be 8-coordinate (Fig. 25), however this would result in the complex having three equivalent acetylacetone molecules, each bonded to the uranium atom through both oxygen atoms. This structure would therefore not be in agreement with the experimentally determined results for $UO_2(ACA)_2 \cdot HACA$.

An X-ray crystallographic study has been performed[48] on $UO_2(ACA)_2 \cdot H_2O$. The geometry of coordination was found to be that of a pentagonal bipyramid with seven oxygen atoms localized at the corners. The pentagonal base of the bipyramid is formed by the four oxygen atoms of the chelate rings and one oxygen atom of the water molecule. The uranyl group was found to be linear. It is proposed in this work that the complex $UO_2(ACA)_2 \cdot HACA$ has a similar structure (Fig. 25), the third acetylacetone molecule being coordinated through one oxygen only, thus giving rise to one uniquely bonded acetylacetone molecule.





(II)

Fig. 25.

Possible structures of $UO_2(ACA)_2 \cdot HACA$

(I) 8-coordinate, (II) 7-coordinate.

SZOKE[92] has reported the formation of $H\left[UO_2(ACA)_3\right]$ *via* a two-stage synthesis, in the first stage of which ammonia was present for pH control. Since ammonia is known to react with $UO_2(ACA)_2$ to form a complex formulated by HAGER[38] on the basis of its microanalysis as the ammonium salt:

$$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)O^-NH_4^+,$$

it is considered probable that the two products are identical.

The complexes prepared in this section of this work by allowing uranyl nitrate hexahydrate to react with HACA and an aliphatic amine were at first considered to be analogous to the ammonium salt formulation above. The work of HAGER involved the preparation of two such complexes, one derived from ammonia and one derived from methylamine. The IR spectrum[44] and heat of solvation[46] of an ammonia adduct formulated $UO_2(ACA)_2 \cdot NH_3$ have been reported but analysis results were not given, and the method used to prepare the compound was identical with the method used by HAGER to produce the ammonium salt, which contains an additional molecule of HACA. From the reaction of uranyl nitrate and HACA with ammonia, a complex was obtained having an IR spectrum identical with that reported by SZOKE for $H\left[UO_2(ACA)_3\right]$, including the presence of bands in the N-H stretching region. While the IR spectrum of this compound could be construed as consistent with the formulation of the ammonium salt, the N-H stretching frequencies are somewhat high for a quaternary ammonium ion. In the present work, compounds of a similar nature were prepared from a large range of primary aliphatic amines. The absence of N-H stretching frequencies in the IR

spectra and the fact that the calculated and found analysis figures did not agree caused serious doubt of the validity of the ammonium salt formulation for these complexes. As in the case of the acetylacetone adduct of $UO_2(ACA)_2$ it was found that these compounds had very small (< 0.5 mho) molar conductances indicating that they are non-electrolytes.

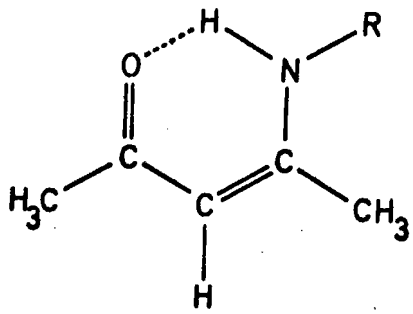
The NMR spectra of these complexes show a signal far downfield of TMS which integrates for one proton. In an ammonium salt, the positive charge on the nitrogen atom would considerably deshield the amino protons, which could give rise to a signal far downfield of TMS. This signal should integrate for three protons whereas in fact it only integrates for one. On addition of D_2O this signal was absent from the NMR spectrum, consequently it must be an active proton, probably bound to a nitrogen or an oxygen atom. Clearly, therefore, the ammonium salt formulation of these complexes is incorrect.

Primary aliphatic amines are known to react with the enol tautomer of HACA with loss of water to form unsaturated β-ketoimines,[100] *e.g.*

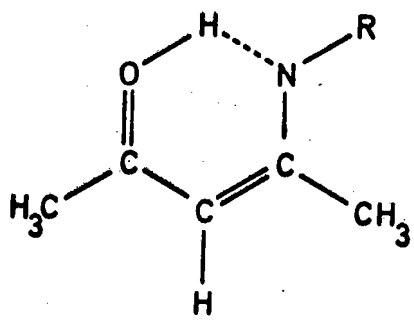
$$H_3C\text{-}CO\text{-}CH{=}C(CH_3)OH + RNH_2 \rightarrow H_3C\text{-}CO\text{-}CH{=}C(CH_3)NHR + H_2O$$

Many β-ketoimines of this type have been prepared,[101-107] and this work extends the preparation of these to include many new compounds. β-Ketoimines can theoretically exist as three possible tautomers (Fig. 26). From the NMR spectra of these compounds it can be demonstrated that they exist predominantly as the tautomer of structure (III).

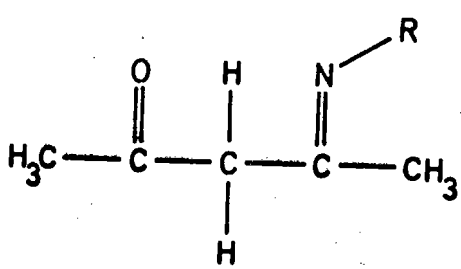
Consider the case where R = CH_3, *i.e.* the β-ketoimine derived from methylamine (Fig. 22). This compound gave NMR



(III)



(IV)



(V)

Fig. 26.

Three tautomeric forms of β-ketoimines.

signals with chemical shifts of 1·92 (3), 1·98 (3), 2·88, 2·97 (3), 4·99 (1) and 10·55 (3) p.p.m. The figures in parentheses represent the number of protons, obtained by integration. The signal at 2·88 and 2·97 p.p.m. is a doublet.

The assignment of these signals is relatively simple if one adopts the supposition (at this stage) that β-ketoimines exist as form (III) of the three possible tautomers. The two signals at 1·92 and 1·98 p.p.m., integrating for three protons each can unambiguously be assigned to the two $C-CH_3$ groups. Differentiation between the two is somewhat more difficult. The methyl group adjacent to the carbonyl group should be deshielded more than the methyl group adjacent to the C-N bond. One is therefore tempted to assign the lower of the two signals (at 1·92 p.p.m.) to the methyl protons adjacent to the carbonyl group, but the shift between them is hardly appreciable, so the above assignment must be regarded as tentative. On D_2O exchange (Fig. 22) these two signals remain unaffected. The doublet centred at 2·92 p.p.m. and integrating for three protons can unambiguously be assigned to the methyl protons of the $N-CH_3$ group. The signal is a doublet due to the splitting of the $N-CH_3$ group resonance by the single proton bound to the adjacent nitrogen atom. On addition of D_2O this signal collapses to a singlet at 2·92 p.p.m. integrating for three protons, since the proton on the adjacent nitrogen atom is now absent, having been replaced by deuterium. The signal at 10·55 p.p.m. integrating for one proton can be unambiguously assigned to the proton bound to the nitrogen atom and hydrogen bonded to the oxygen atom. Its position far downfield of TMS is characteristic of hydrogen-bonded protons; also, on addition of D_2O this signal disappears

completely, indicating that the hydrogen atom is acidic. Finally the signal at 4·99 p.p.m., integrating for one proton must be due to the olefinic proton, if not by virture of the fact that this is the region in which olefinic proton signals are generally found in NMR spectra and that on addition of D_2O the signal remains unchanged, then certainly by the fact that it is the only signal remaining in the spectrum, with only one proton in the compound unaccounted for. Since no other signals are observed in the NMR spectrum it follows that the compound does not exist as a mixture of tautomers, and since the assignments as presented above are only applicable to structure (III), it follows that β-ketoimines exist predominantly in one specific tautomeric form.

The NMR spectra of the deuterated compounds were obtained immediately after addition of D_2O to the deuterochloroform solution of the compound. All spectra were redetermined after twenty-four hours had elapsed, when it was found that they were unchanged with the exception of that of the β-ketoimine derived from n-butylamine. The spectrum of this compound showed that the olefinic proton had been replaced by deuterium. This compound would therefore appear to be similar to acetoacetic ester, in which the olefinic protons are activated by the electron withdrawing carbonyl groups.

The IR spectra of the β-ketoimines (Fig. 10) also support the structure as outlined above on the basis of the NMR spectra. All the β-ketoimines prepared for this study, with the exception of the one derived from ammonia, displayed a lack of N-H stretching frequencies in the expected region (near 3300 cm^{-1}). The N-H band has probably been broadened by hydrogen bonding and lowered

to about 3000 cm^{-1} where it is hidden by the C-H stretching modes. The β-ketoimine derived from ammonia displays νN-H at 3358 and 3192 cm^{-1} since the compound possesses a free N-H as well as a hydrogen-bonded N-H. This free N-H gives rise to a signal in the NMR spectrum at 5.53 p.p.m. which disappears on the addition of D_2O.

All the β-ketoimines exhibit two strong bands in the IR between 1550 and 1630 cm^{-1}. The high frequency band centres around 1620 cm^{-1}, and is assigned to νC=O. The C=O stretch normally lies between 1540 and 1640 cm^{-1} for β-ketoimines.[108] The low frequency band occurs near 1580 cm^{-1} and is assigned to νC=C. The C=C stretch for a C=C bond conjugated with a carbonyl group is normally found near 1600 cm^{-1}.[108]

To confirm the results so far discussed, the β-ketoimines derived from dimethylamine and diethylamine were prepared. In these compounds no hydrogen bonding is possible, hence the compound can only have the following structure:

$$H_3C\text{-}CO\text{-}CH{=}C(CH_3)NRR$$

The NMR spectra of these compounds display no downfield signal as did the β-ketoimines derived from primary aliphatic amines, thus giving further evidence that that signal was due to the hydrogen-bonded proton. The signal caused by the olefinic proton occurs at almost exactly the same position as for the previous compounds. Of interest is the fact that the signals due to the $C\text{-}CH_3$ groups are much further apart than in the monoalkylimines. This can be rationalized by proposing that cyclization accompanying hydrogen bonding leads to a certain degree of pseudo-aromatic character, the two $C\text{-}CH_3$ groups becoming more or less equivalent. When hydrogen bonding does not occur,

the two C-CH_3 groups are in very different situations. This accounts for the greater degree of separation of the two signals. On addition of D_2O no change occurs in the spectra, indicating the absence of active protons.

The IR spectra of the dialkylimines exhibit two strong bands between 1550 and 1650 cm^{-1}. The high frequency band is found near 1640 cm^{-1}, slightly higher than $\nu C=O$ of the monoalkylimines. This is probably due to the fact that there is no hydrogen bonding present. Hydrogen bonding causes $\nu C=O$ to be lowered.[108] The second band appears similar to that discussed previously and is assigned to $\nu C=C$. These two bands are separated by 70 cm^{-1} as opposed to a separation of 40 cm^{-1} in the case of the monoalkylimines. This can be explained on the basis of electron delocalization in the cyclic hydrogen-bonded form. This would lead to coupling between $\nu C=O$ and $\nu C=C$. In the case of the dialkylimines the integral path of the electrons is not increased due to the fact that cyclization cannot occur, therefore $\nu C=O$ and $\nu C=C$ represent the fundamental vibrational modes.

In the light of what is now known about the acetylacetone adduct of $UO_2(ACA)_2$ and the β-ketoimines, it would appear that the complexes derived from the reaction of uranyl nitrate hexahydrate with acetylacetone and a primary aliphatic amine are β-ketoimine adducts of $UO_2(ACA)_2$. These probably arise from the reaction:

$$UO_2(NO_3)_2 \cdot 6H_2O + 3HACA + RNH_2 \rightarrow$$

$$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH=C(CH_3)NHR + 2HNO_3 + 7H_2O$$

This postulation was verified by preparing the β-ketoimine adducts of $UO_2(ACA)_2$ by recrystallizing $UO_2(ACA)_2 \cdot H_2O$ from the β-ketoimine.

The products of this reaction proved to be identical to the complexes prepared by the original method. These complexes probably have a similar structure to $UO_2(ACA)_2 \cdot HACA$, *i.e.*, pentagonal bipyramidal, the β-ketoimine being bound directly to the uranium atom. There are two possible ways in which the β-ketoimine may be coordinated to the uranium atom, either through the oxygen atom, or through the nitrogen atom. An X-ray crystallographic study on the complex

$$UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)NH_2$$

has been instigated in this department to determine the nature of the bonding in these complexes.

The analysis figures for carbon, hydrogen, nitrogen and uranium agree with the $UO_2(ACA)_2 \cdot$β-ketoimine formulation of these complexes. In fact HAGER'S reported analysis figures[38] for carbon, hydrogen, ammonia and uranium for the proposed ammonium salt formulation show better agreement with the β-ketoimine adduct formulation than his original proposal.

The IR spectra of these compounds (Fig. 11) also support the $UO_2(ACA)_2 \cdot$β-ketoimine formulation. In all complexes of acetylacetone there are two strong bands between 1500 and 1600 cm^{-1} which have been assigned, the lower to νC=C, the higher to νC=O (see Introduction). In $UO_2(ACA)_2 \cdot H_2O$ these bands occur at 1525 and 1585 cm^{-1} respectively. The spectra of the β-ketoimine adducts show, in addition to these two bands which occur near 1527 and 1580 cm^{-1}, two additional peaks in this region, one around 1555 cm^{-1}, the other around 1605 cm^{-1}. These are assigned to νC=C and νC=O respectively of the adducted β-ketoimine molecule. These bands occur at higher wavenumber than the similar bands of the chelated HACA molecule since the β-ketoimine is less strongly

bound to the uranium atom than the acetylacetone molecule. The C=C and C=O bonds are therefore strengthened at the expense of the U-imine bond. A very strong broad band is observed at approximately 1335 cm^{-1}. This band is absent in the spectra of $UO_2(ACA)_2 \cdot H_2O$ and $UO_2(ACA)_2 \cdot HACA$, and is therefore probably an imine (ligand) vibration. C-N stretching vibrations have been reported[108] for primary aliphatic amines near 1400 cm^{-1}, therefore this band is assigned to νC-N of the imine molecule. The wavelength of absorption of this mode was found to be substituent-sensitive. Electron releasing groups strengthen the bond whereas electron withdrawing groups weaken it. A very strong band at around 1270 cm^{-1} is present in all spectra, including those of $UO_2(ACA)_2 \cdot H_2O$ and $UO_2(ACA)_2 \cdot HACA$. This has been assigned[82] as a coupled (δC=C + νC-CH_3) mode of the coordinated acetylacetone molecule. A very weak band observed at approximately 1212 cm^{-1} in all spectra has been assigned[82] as δC-H i.p. of the coordinated HACA molecule. A strong band occurs in most of the imine adduct spectra around 1080 cm^{-1}. This band is absent in the spectra of $UO_2(ACA)_2 \cdot H_2O$ and $UO_2(ACA)_2 \cdot HACA$, and is therefore ascribed to an imine mode. Primary aliphatic amines have been reported[108] to absorb at 1020-1220 cm^{-1} due to νC-N, however the coordinated HACA molecule displays an absorption in this region around 1020 cm^{-1}, assigned[82] as a CH_3 rocking mode. The peak which centres at 1080 cm^{-1} may, therefore, be tentatively assigned to one of these two modes. A band of moderate intensity (sometimes a shoulder) is observed near 925 cm^{-1}. This has been assigned[82] as a coupled (νC=O + νC-CH_3) mode of the coordinated acetylacetonate. A very strong sharp band (generally

the strongest band in the spectrum) is observed at approximately 905 cm^{-1}. This has been assigned[39] as νU=O asym. The fact that there is no symmetric stretching mode observable in any of the spectra indicates that the uranyl group is linear. Two peaks observed at about 800 and 760 cm^{-1} have been assigned[82] as δC-H o.o.p. modes of the coordinated HACA molecule.

Assignments of peaks observed below 700 cm^{-1} is difficult since many skeletal vibrations occur in this area. Bands occurring at around 523 and 405 cm^{-1} would appear to be due to variously coupled νU-O modes (See section (3) of Discussion).

Two bands at about 625 and 545 cm^{-1} are observed only in the imine adducts. The bands are both weak and can therefore probably be ascribed to U-imine modes. If this assignment is correct, then it is probable that the imines are coordinated to the uranium atom *via* the oxygen atom. Metal to oxygen stretching modes generally absorb between 400 and 600 cm^{-1}, whereas νM-N is generally found at lower wavenumbers.[110] A weak band occurring at about 455 cm^{-1} is found only in the spectra of the monoalkylimine adducts. This band is probably due to some ring deformation mode of the cyclic imine molecule. A very weak band found near 350 cm^{-1}, occurring only in the imine adducts, is ascribed to a U-imine mode. The possibility of this band being due to νU-N cannot be ignored. Finally, a very strong band occurring in all complexes at about 270 cm^{-1} has been assigned[49] to a bending vibration of the uranyl group (δO=U=O).

The NMR spectra of these compounds (Fig. 23) are also consistent with the $UO_2(ACA)_2 \cdot$β-ketoimine formulation. The NMR spectra will be discussed separately on the basis of the formula $UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)NHR$ as each spectrum is very different, depending upon the nature of R. Common to the NMR spectra of

all compounds were signals at approximately 2·1(3), 2·3(12), 2·5(3), 5·3(1), 5·8(2) and 11·5 p.p.m. (1). These signals are assigned to N-C-CH_3, CH_3 of ACA rings, O=C-CH_3, C-H, C-H of ACA rings and N-H···O respectively, on the same basis as the assignments of the signals of the uncoordinated β-ketoimines and by comparison with the NMR spectrum of $UO_2(ACA)_2$.

R = C_6H_5 The NMR spectrum of this compound shows the six signals mentioned above and a complex peak at about 7·1 p.p.m. which integrates for five electrons. This signal is due to the five aromatic protons of the phenyl ring. On addition of D_2O this signal shows no change; the far downfield signal disappears.

R = H The NMR spectrum of this compound shows the six basic signals plus one other at 5.82 p.p.m. integrating for one proton. This is due to the non-hydrogen-bonded proton bound to the nitrogen atom. On addition of D_2O both this signal and the far downfield signal disappear.

R = CH_3 In addition to the six basic signals a doublet is observed at 2·94, 3·03 p.p.m. (3). This is due to the splitting of the N-CH_3 group resonance by the single proton bound to the adjacent nitrogen atom. On substitution of deuterium for this proton the doublet collapses to a singlet at 2·98 p.p.m. (3).

R = C_2H_5 Signals due to the ethyl group are apparent at 1.03 p.p.m. (3) in the form of a triplet due to CH_3 and at 3.35 p.p.m. (2) in a complex second order pattern due to CH_2. On addition of D_2O the triplet remains unchanged but the complex pattern collapses to a well defined quartet centred at 3.55 p.p.m. (2) due to removal of the proton on the adjacent nitrogen atom.

R = n-C_3H_7 In this compound a triplet is observed at 0.75 p.p.m. (3) due to the CH_3 group, a complex pattern at 1·42 p.p.m. (2) due to the CH_2 group adjacent to the CH_3 group and a complex pattern at 3·23 p.p.m. (2) due to the CH_2 group adjacent to the nitrogen atom. On addition of D_2O the triplet and the complex pattern at 1·42 p.p.m. remain unchanged, but the complex pattern at 3·23 p.p.m. collapses to a triplet at 3·25 p.p.m. (2) since the signal is now only split by the two protons on the adjacent carbon atom.

R = i -C_3H_7 A doublet centred at 1·06 p.p.m. (6) is due to the two equivalent CH_3 groups. The splitting is due to the effect of the single proton on the adjacent carbon atom. A very complex pattern is observed at 3·75 p.p.m. (1) which is due to CH. On addition of D_2O the doublet is unchanged and the very complex pattern collapses to a less complex pattern. The reason for the complexity is the fact that the CH signal is split by six protons on the adjacent carbon atoms.

R = n-C_4H_9 Very complex patterns are observed for the $CH_3CH_2CH_2$ part of the molecule which do not change on addition of D_2O. A complex pattern observed at 3·28 p.p.m. (2) due to the CH_2 adjacent to the nitrogen atom collapses to a triplet on addition of D_2O.

R = i-C_4H_9 A doublet centred at 0·77 p.p.m. (6) due to the two CH_3 groups and a complex pattern at 1·90 p.p.m. (1) due to the CH do not change on addition of D_2O. A triplet at 3·14 p.p.m. (2) due to the CH_2 adjacent to the nitrogen atom collapses to a doublet on addition of D_2O.

$\underline{R = t\text{-}C_4H_9}$ A signal at 1·32 p.p.m. (9) due to the three equivalent CH_3 groups was unchanged on addition of D_2O.

Since tertiary aliphatic amines are incapable of forming β-ketoimines, it was considered to be of interest to examine the complexes formed if the original method of preparation was repeated using triethylamine and trimethylamine in place of a primary aliphatic amine. In both cases the simple adducts $UO_2(ACA)_2 \cdot NR_3$ ($R = CH_3, C_2H_5$) were obtained.

R	Calculated				Found			
	%C	%H	%N	%U	%C	%H	%N	%U
CH_3	29.6	4.4	2.7	45.2	29.9	4.1	2.6	45.0
C_2H_5	33.8	5.1	2.5	41.8	34.1	5.4	2.6	41.5

The IR spectra of these compounds showed no doubling of νC=O and νC=C which would be expected if an additional molecule of HACA were present. The NMR spectra were consistent with the simple adduct formulation as above.

These considerations lead to the question of whether simple adducts of the type $UO_2(ACA)_2 \cdot RNH_2$ are capable of being synthesised. The compound formulated in two papers [44,46] as $UO_2(ACA)_2 \cdot NH_3$ is almost certainly the β-ketoimine adduct since it was prepared by HAGER'S method, analyses were not reported, and the published IR spectrum[44] is identical to that described herein for the complex $UO_2(ACA)_2 \cdot H_3C\text{-}CO\text{-}CH{=}C(CH_3)NH_2$. All attempts in this laboratory to prepare $UO_2(ACA)_2 \cdot RNH_2$ using a large variety of amines have met with no success, the β-ketoimine adducts being obtained under a variety of conditions. By contrast, it has been found that under similar experimental conditions uranyl dibenzoylmethanate yields only the simple adduct $UO_2(DBM)_2 \cdot RNH_2$, the β-ketoimine adduct not forming at all.

2. PRIMARY ALIPHATIC AMINE ADDUCTS OF URANYL DIBENZOYLMETHANATE

In contrast to uranyl acetylacetonate it has been found that primary aliphatic amines react with $UO_2(DBM)_2$ to form adducts of the type $UO_2(DBM)_2 \cdot RNH_2$. Although these complexes were prepared by adding the amine to an ethereal solution of $UO_2(DBM)_2 \cdot H_2O$, it was found that they could be prepared by adding a mixture of the amine and HDBM in methanol to a methanolic solution of uranyl nitrate hexahydrate, and heating the mixture on a water bath. If the ligand is HACA, both of these methods result in the appropriate β-ketoimine adduct of $UO_2(ACA)_2$. It has been reported[111-112] that HDBM does form β-ketoimines of a similar nature to those derived from HACA, however the more drastic conditions required to prepare them is probably the reason why they do not form under the conditions described above. It would appear that $UO_2(DBM)_2$ is more stable than $UO_2(ACA)_2$, since addition of a primary aliphatic amine to a solution of the latter causes some of the complex to decompose, forming the β-ketoimine which then adducts onto the remaining $UO_2(ACA)_2$ and precipitates.

The $UO_2(DBM)_2 \cdot RNH_2$ complexes described in this section (Fig. 12) are all mono adducts and probably have pentagonal bipyramidal structure on the basis of that established for $UO_2(ACA)_2 \cdot H_2O$.[48] The ammonia adduct of $UO_2(DBM)_2$ has previously been described.[43]

A plot of $\nu U{=}O$ against the σ^* values of TAFT (Fig. 27) for the primary aliphatic amines shows that electron withdrawal by the amine results in a weakening of the U=O bond. This is the opposite of what has been found for electron withdrawal from the

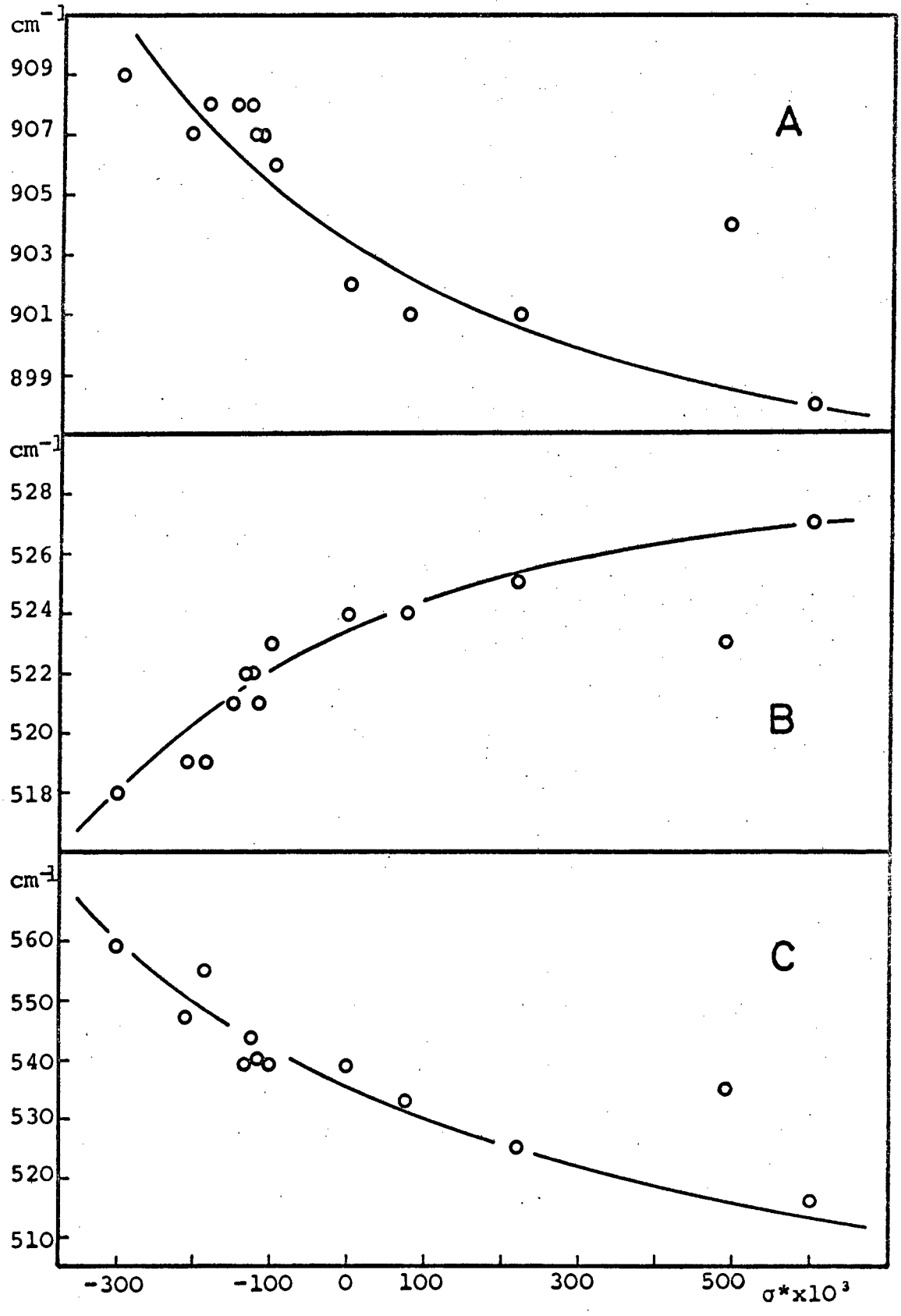
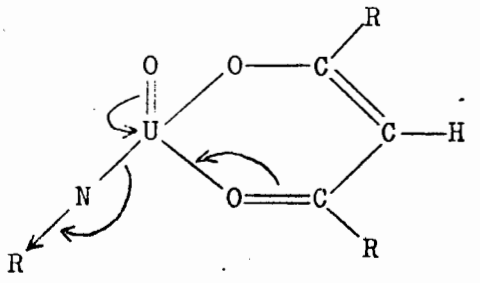


Fig. 27.

Relationship between σ* and
A; νU=O, B; νU-O, C; νU-N
for the complexes $UO_2(DBM)_2 \cdot RNH_2$

β-ketoenolate ring (see next section). δO=U=O is observed around 270 cm^{-1} and shows no shifts parallel to νU=O. The two bands observed at 430 and 455 cm^{-1} which have been tentatively assigned to variously coupled U-O modes show little shift with change of amine. The band observed at around 523 cm^{-1} and assigned to νU-O displays a trend with change of amine (Fig. 27), indicating that the U-O bond is strengthened on electron withdrawal by the amine. A similar situation has been shown to exist in a series of primary aliphatic amine adducts of zinc(II) acetylacetonate.[113] A plot of νU-O against νU=O, although not linear, indicates strengthening of the U=O bond at the expense of the U-O bond.

A completely new feature of the far IR spectra of these complexes compared with other adducts of $UO_2(DBM)_2$ (to be discussed in the next section) is the appearance of a peak of weak to medium intensity at around 535 cm^{-1}, displaying a definite trend with change of amine (Fig. 27). The shifts of this peak are parallel with the shifts of νU=O, indicating a decrease in the strength of the bond with increased electron withdrawal by the amine. One possible assignment of this peak is that it is a coupled νU=O mode, however, the fact that no other peak of this nature has been observed in other $UO_2(DBM)_2$ adducts would appear to indicate that this assignment is incorrect. Another possible assignment of this peak is that it is a coupled νU-N mode. The fact that this peak displays an inverse linear relationship to νU-O is a good indication that it may be due to a νU-N mode. On the basis of the observations made above it would appear that electronic shifts of the following nature may be postulated for these complexes:



i.e. electron withdrawal by the substituent R results in weakening of the U=O and U-N bonds and strengthening of the U-O bond.

An examination of νN-H at approximately 3260 and 3330 cm^{-1} showed no trend with σ*, probably because the proximity of the substituent to the N-H bonds enhances the mass effect. This conclusion is supported by the fact that νN-H sym. has a minimum value for the substituent of lowest mass (R=H). It can be seen from Fig. 27 that the point for the complex $UO_2(DBM)_2 \cdot NH_3$ always falls well off the line. Once again this is probably due to the mass effect.

In an attempt to substantiate the above conclusions, the synthesis of a series of primary aliphatic amine adducts of uranyl *p,p'*-dimethoxydibenzoylmethanate was attempted. Only three adducts could be prepared, those of aniline, methylamine and t-butylamine. The reason for the non-adduction of the other amines is difficult to explain, since the three amines above cover the widest possible range of σ* values, indicating that electronic effects are not an influencing factor in the mode of adduction. The methyl group is relatively small compared with the phenyl and t-butyl groups, consequently steric effects also seem to be of little importance in determining adduct formation.

Inspection of the IR spectra of these compounds (Fig. 13) would seem to indicate that a plot of νU=O against σ* yields a relationship of the same type as that obtained for the analogous complexes derived from HDBM. No one band in the far IR spectra could be assigned to νU-O or νU-N, since this region of the spectrum is very complex, probably due to various substitution patterns.

A correlation between the chemical shift of the amino protons and σ* has been reported[113] for a series of primary aliphatic amine adducts of zinc(II) acetylacetonate. In the hope of finding a similar relationship, an NMR study of the complexes prepared in this section was instigated. The compounds are all soluble in deuterochloroform. It was found that the signal due to the amino protons was very broad, ranging over approximately 1 p.p.m., with consequent difficulty in obtaining a precise value of the signal position. Integration of the NMR spectra indicates that the complexes are mono adducts, confirming microanalytical results. The internal similarities of the IR spectra of these compounds suggest that they are isostructural.

3. VARIOUSLY SUBSTITUTED URANYL β-KETOENOLATES

Recently[114] the effect of varying the chelate ring substituents on the IR spectra of metal β-ketoenolates has been determined in this laboratory. It was concluded that the electronic effect of the substituent is associated with its field and resonance contributions. Strongly electron withdrawing substituents produce low νM-O and high νC=O. Electron releasing substituents reverse the relationship. The same effects are observed for a wide variety of transition and non-transition metal ions. Metal ions employed were K(I), Al(III), Cu(II), Sc(III), V(III), Cr(III) and Fe(III).

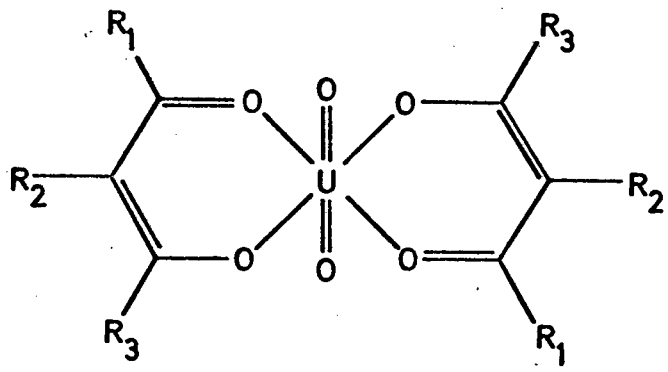
A study of substituent effects on the IR spectra of dioxouranium(VI) complexes, which is the subject of the present section, may be approached from three points of view;

(i) The effect of varying the chelate ring substituent (R_1, R_2, R_3; formula I, II, III; Fig. 28) in uranyl β-ketoenolate complexes.

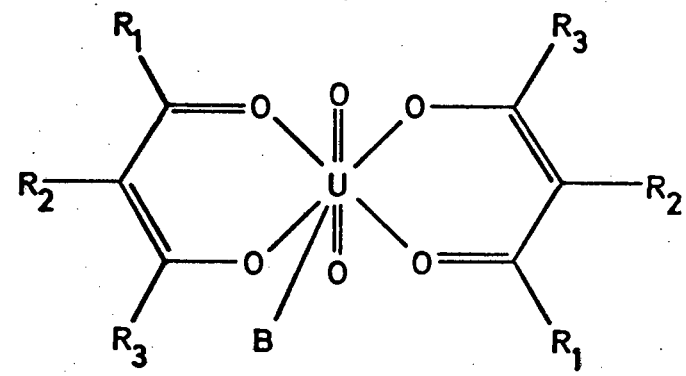
(ii) The effect of varying the nature of the adducted base (B; formula II; Fig. 28).

(iii) The effect of varying the substituent on the adducted base (R; formula III; Fig. 28).

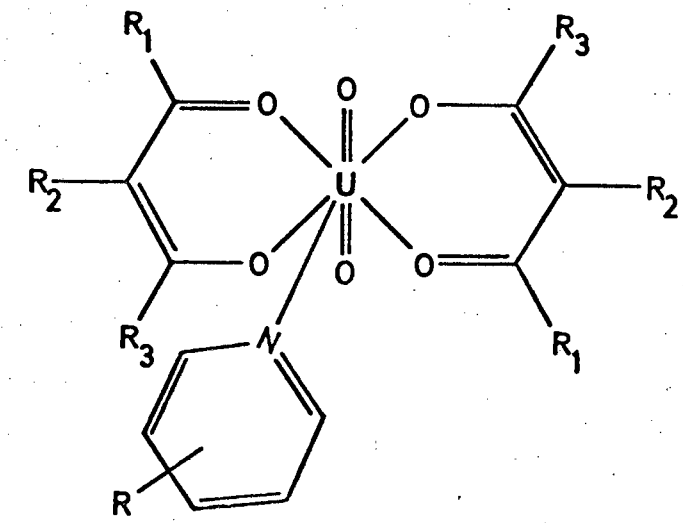
This work is largely restricted to an examination of the effect of substituents on νU=O since this is the only vibration of significance which can be reliably assigned in the IR spectra. (For representative examples of IR spectra see



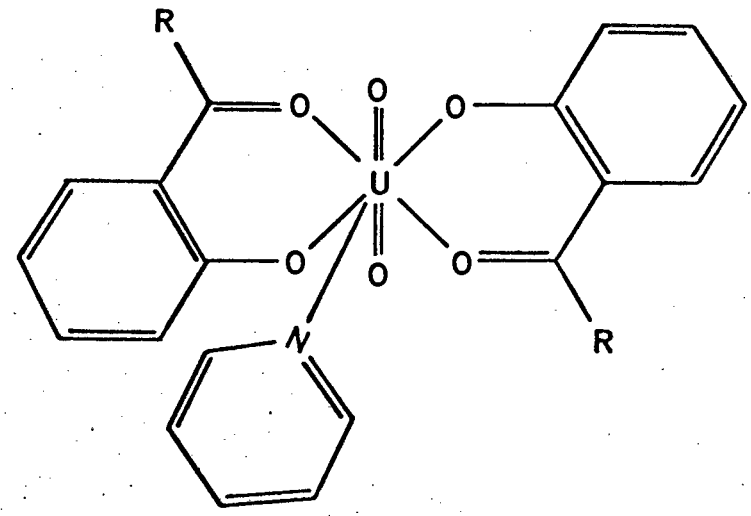
(I)



(II)



(III)



(IV)

Fig. 28.

Figs. 1-9). Theoretically, if the O=U=O species is linear, only the asymmetric U=O stretching mode should be observable in the IR spectra. All available X-ray crystallographic evidence points to linearity of the uranyl group but there is also evidence that in some uranyl complexes the symmetric vibration becomes weakly allowed so that in these cases both bands are observable.[115-116] It may be expected that νU=O will be influenced by the electronic effects of the substituents R_1, R_2 and R_3 but there seems to be no *a priori* reason for assuming that this frequency will be increased or decreased by (say) electron releasing substituents. Furthermore, the effect on νU=O will be the resultant of the independant field and inductive effects of these substituents on the uranyl bond.

It has been shown by SWAIN and LUPTON[117] that a substituent effect may be expressed in the form

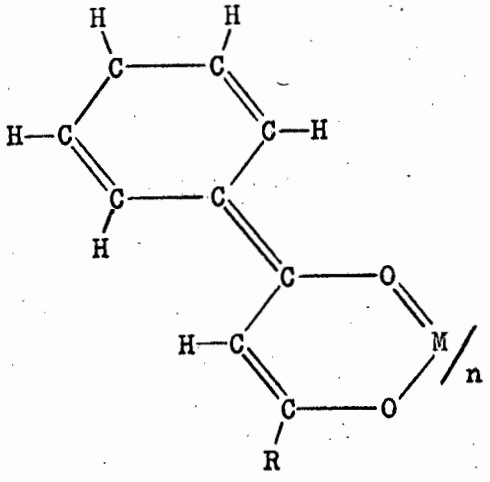
$$\sigma = fF + rR \qquad (1)$$

where F and R are field and resonance parameters and f and r are coefficients which determine the relative weightings of the field and resonance contributions appropriate to the system being examined. For disubstitution in the chelate ring the following relationship may be employed

$$\Sigma\sigma = (fF)_{R_1} + (fF)_{R_2} + (rR)_{R_1} + (rR)_{R_2} \qquad (2)$$

to represent the combined field and resonance effects of both substituents, since there is considerable justification for assuming the additive nature of substituent effects.[5-6] In calculating values of $\Sigma\sigma$ some assumption has to be made regarding the magnitude of f and r. Previous work[114] has shown that the

assumption f = 0·75, r = 0·25 yields values of Σσ which decrease monotonically with increasing νM-O in a series of copper(II) β-ketoenolates except for phenyl substituents. Phenyl substituents are capable of strong resonance interaction of the quinonoid type



not possible with other substituents. Therefore it seems reasonable to suppose that r is greater for complexes with phenyl substituents. Use of f = 0·25, r = 0·75 for benzoylacetonates and f = 0, r = 1·00 for dibenzoylmethanates produces values of Σσ which are consistent with the order of νCu-O (Table 1). Also listed in Table 1 are the corresponding data for the uranyl complexes now under discussion.

Table 1 shows that, generally, νU=O decreases with Σσ, *i.e.* the U=O bond is weakened by substituents with resultant electron releasing effects. The deviation from the relationship of the νU=O values for the complexes derived from HPVA and HDPM may be due to steric factors conferred upon the molecule by the bulky tertiary butyl groups. Conversely, it can be seen that

νCu-O increases as $\Sigma\sigma$ decreases, *i.e.* the Cu-O bond is strengthened by electron releasing substituents. This is the precise opposite of what is observed in the primary aliphatic amine adducts of $UO_2(DBM)_2$ (see previous section), where it was found that electron release by the substituent exocyclic to the chelate ring resulted in strengthening of the U=O bond.

Unfortunately νU-O (as opposed to νU=O) cannot be reliably assigned for the full series of uranyl β-ketoenolates. It would appear from a limited number of complexes of the type $UO_2(L)_2 \cdot py$ that a similar situation to the copper complexes obtains:

L	TFA	ACA	BZA	DBM	DPM	
Coupled νU-O	408	403	412	453	486	cm^{-1}

i.e. the strength of the U-O bond is increased with increased electron release into the ring. Under these circumstances it can be concluded that substituents affect νU=O and νU-O conversely, the U=O bond is strengthened at the expense of the U-O bond.

The relationship between νU=O and νC=O for the various series of complexes $UO_2(L)_2 \cdot B$ is shown in Fig. 29. νU=O and νC=O increase or decrease simultaneously on changing the nature of the substituent on the β-ketoenolate ring. By extrapolating to zero the intercepts of the curves were determined. It was found possible to relate νU=O and νC=O for each adduct by applying the following equations:

Anhydrous complexes	$\nu C{=}O = \nu U{=}O + 636$	cm^{-1}
Water adducts	$\nu C{=}O = 6\nu U{=}O - 3950$	cm^{-1}

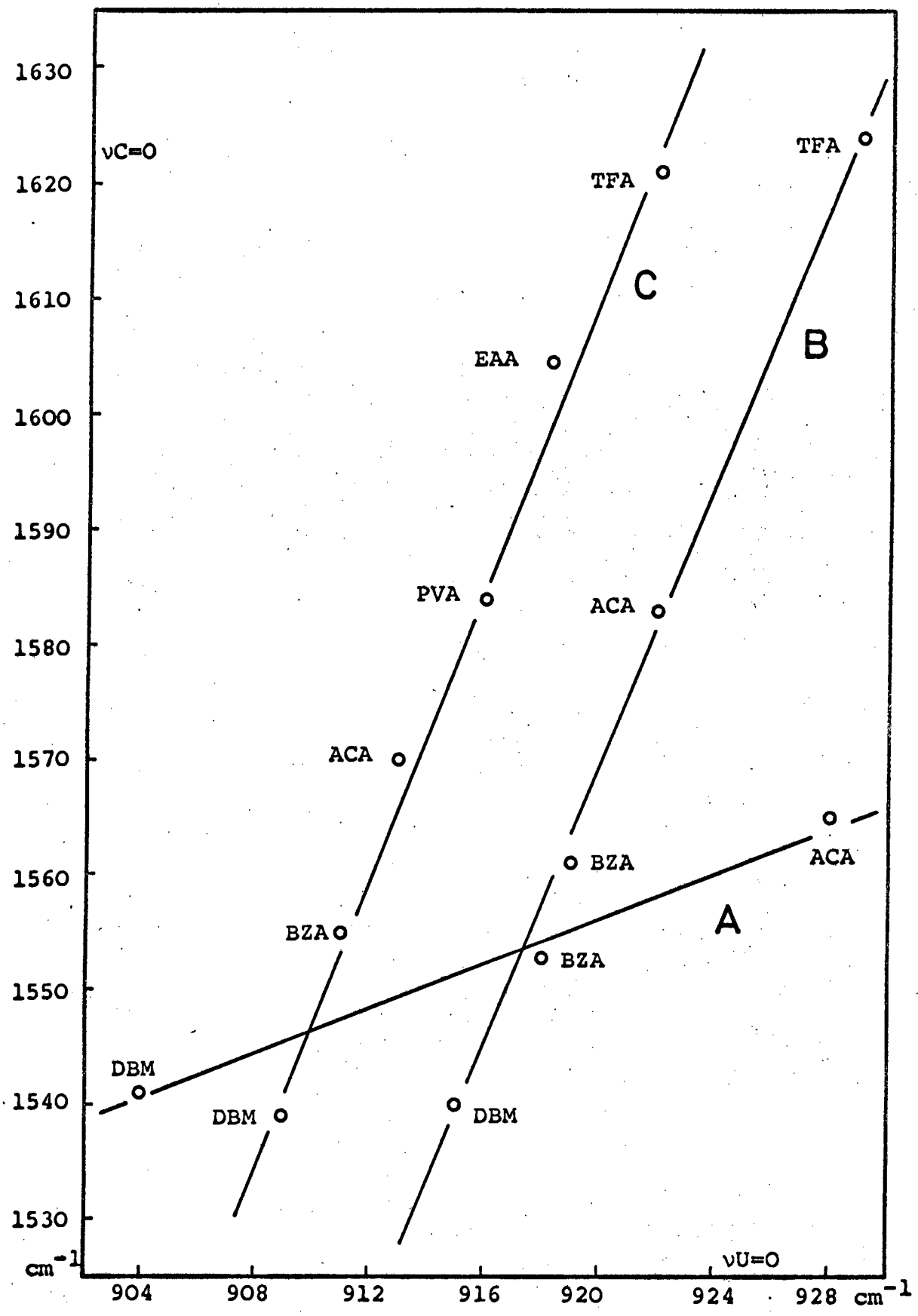


Fig. 29.

Relationship between νC=O and νU=O
for complexes of the type $UO_2(L)_2 \cdot B$.
A; B = nil, B; B = H_2O, C; B = C_5H_5N.

Pyridine adducts $\nu C{=}O = 6\nu U{=}O - 3911\ cm^{-1}$

If the field effect of the substituent is more significant with respect to determining the strength of the U=O bond, it may be expected that the shift of νC=O would exceed that of νU=O. This is found for the water and pyridine adducts. The shifts of νU=O and νC=O are very similar for the anhydrous complexes, suggesting that a larger proportion of the electronic effect is transmitted *via* the resonance effect. It has been suggested earlier that the phenyl groups lead to a major contribution of the quinonoid resonance form. In this form the C=O bond order is reduced, and the complexes derived from HBZA and HDBM exhibit the lowest νC=O as expected. Electron withdrawal by the chelate substituent causes a simultaneous increase of νU=O and νC=O. This suggests that substituents of this type (*e.g.* CF_3) cause a delocalization of the oxygen lone pairs into both the C=O and U=O bonds, thus the electronic effect of the substituent is transmitted through the uranium atom.

In an attempt to verify the above results a series of pyridine adducts of uranyl *o*-hydroxyarylcarbonyl compounds was prepared (Formula IV, Fig. 28). The IR spectra of these complexes (Fig. 8) confirmed the β-ketoenolate results, *i.e.* νU=O and νC=O were simultaneously increased or decreased depending upon the electronic nature of the substituent on the chelate ring. The carbonyl absorption in the IR spectrum has the form of a strong band with a high frequency shoulder. The wavelength of absorption of the strong band and the shoulder are plotted in Fig. 30. As with the β-ketoenolates it was possible to relate νC=O and νU=O by applying the following equations:

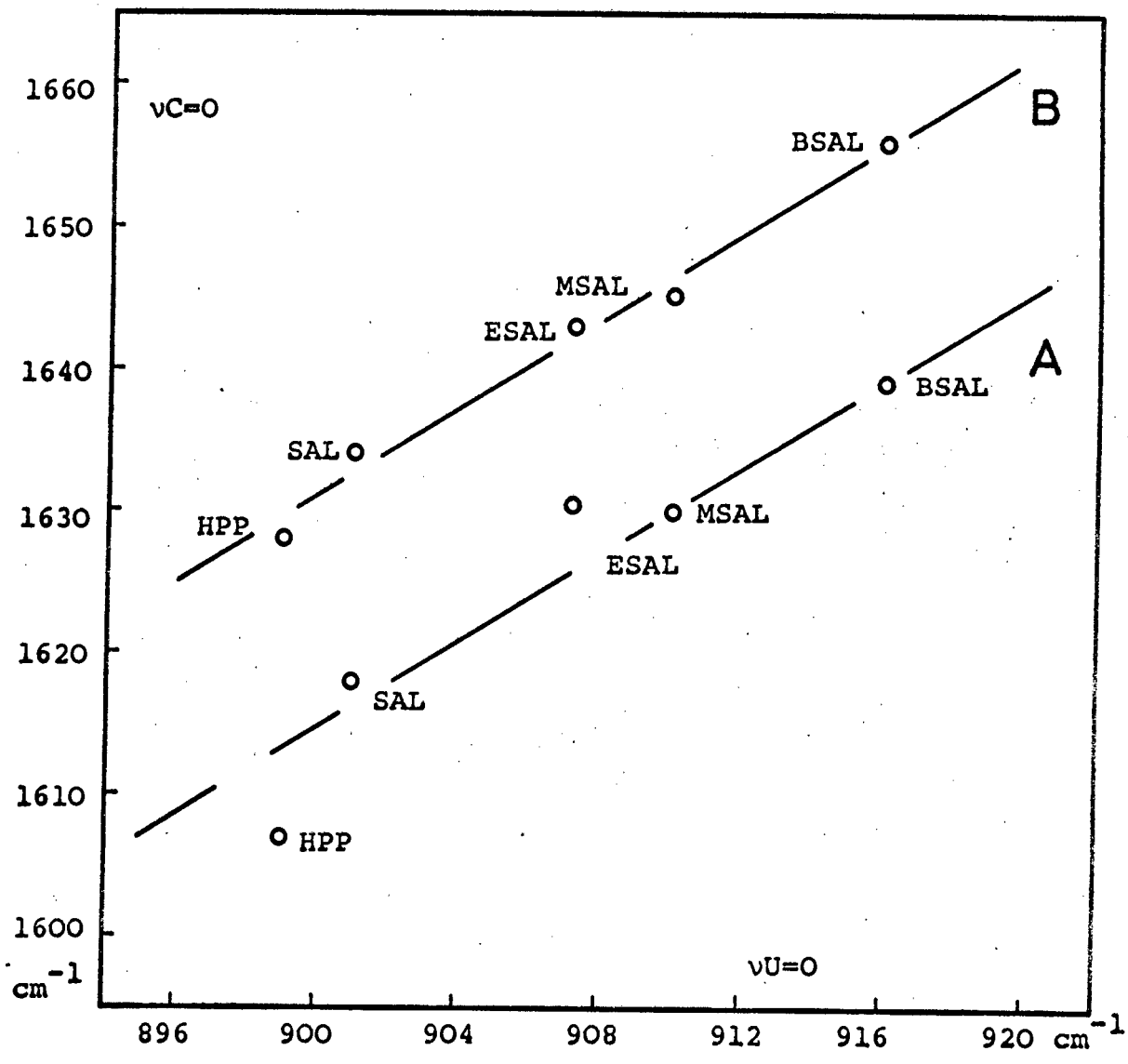


Fig. 30.

Relationship between νC=O and νU=O
for complexes of the type $UO_2(L)_2 \cdot py$.
A = Strong band, B = shoulder.

Shoulder	$\nu C{=}O$	=	$1.6\nu U{=}O$	+	190 cm^{-1}
Strong band	$\nu C{=}O$	=	$1.6\nu U{=}O$	+	173 cm^{-1}

Although the results found are in agreement with those found for the β-ketoenolates, the slope is different. In these complexes $\nu C{=}O$ and $\nu U{=}O$ display shifts of approximately the same magnitude, whereas $\nu C{=}O$ of the β-ketoenolate pyridine adducts displays a much greater shift than $\nu U{=}O$ on varying the chelate ring substituent. This is probably due to the fact that the aromatic ring gives rise to bond fixation of the C=C bond and consequently also the C=O bond. The electronic effect of the substituent will not, therefore, cause such a dramatic change of $\nu C{=}O$ as it does in the case of the β-ketoenolates.

The order of increasing $\nu U{=}O$ in the pyridine adducts of uranyl *o*-hydroxyarylcarbonyl compounds is:

$$R = C_2H_5 < H < OC_2H_5 < OCH_3 < OC_6H_5.$$

Since there is a certain amount of bond fixation in the chelate ring, it would be expected that the electronic effect of the substituent would be transmitted mainly by field effects. This is verified by scrutiny of the *F* and *R* values[117] of the substituents in Table 2.

TABLE 2.

R	*F*	*R*	f	r	σ	$\nu U{=}O$ cm^{-1}
C_2H_5	-0.07	-0.11	0.75	0.25	-0.08	899
H	0	0	-	-	0	901
OC_2H_5	+0.36	-0.44	0.75	0.25	+0.16	907
OCH_3	+0.41	-0.50	0.75	0.25	+0.19	910
OC_6H_5	+0.75	-0.74	0.75	0.25	+0.54	916

It is apparent that the use of f = 0.75, r = 0.25 as in the case of the analogous β-ketoenolate complexes produces σ values of the appropriate order of νU=O, however it would appear that use of f = 1·00, r = 0 would give an even better agreement in terms of relative electronic effect.

A study of the far IR spectra of the *o*-hydroxyarl-carbonyl complexes was made in an attempt to assign νU-O. Only one substituent-sensitive band was found in this region. Since this band displays shifts parallel to both νC=O and νU=O, it probably comprises coupling of one or both of these vibrations with some other vibration.

An extensive study[115] of the effects of ligation on νU=O in a series of complexes of uranyl nitrate of general formula $UO_2(NO_3)_2L_2$ has been reported. It was found that ligands L of high ligand field strength caused a reduction in νU=O. Quantitative measurements of ligand field strength now available[118] (JORGENSEN'S f parameters) enable us to show that, with one exception (L = pyridine), there is a monotonic decrease in νU=O as f increases:

L	F	H_2O	NCS	py	NH_3	en	CN	
f	0.90	1.00	1.03	1.25	1.25	1.28	1.70	
νU=O	960	945	898	926	895	888	873	cm^{-1}

The study showed that the decrease in νU=O is given by

$$\Delta\nu = -\text{electrostatic effect} - \sigma(L \rightarrow M) - \pi(L \rightarrow M) \pm \pi(M \rightarrow L) \qquad (3)$$

where the $\sigma(L \rightarrow M)$ term predominates. Those ligands for which

metal-ligand π-bonding is important, *e.g.* pyridine, would be displaced towards smaller $\Delta\nu$ (higher νU=O) if the last term in the equation has positive sign. It is the capacity which pyridine has for entering into such bonding (compared with ammonia) which is considered to produce the anomalous position of the pyridine complex in the order of νU=O values.

For this reason it was considered to be of interest to determine the effect of substitution of the pyridine ring in a series of complexes $UO_2(ACA)_2 \cdot R\text{-}C_5H_4N$. A series of twenty-six complexes was prepared and νU=O determined. The IR spectra of the free pyridines were determined in order to be able to eliminate pyridine bands from the spectra of the complexes. Furthermore, some substituted pyridine complexes of zinc(II) chloride were prepared and their IR spectra determined in order to observe the positions of the pyridine bands when coordinated to a metal ion.

The electronic effect of the pyridine substituents (as determined by their substituent parameters, σ) failed to cause an appreciable shift of νU=O for electron withdrawing substituents but electron releasing substituents shifted νU=O to lower wavenumber. There was an overall increase of 19 cm^{-1} between the extremes of the strongly electron releasing 4-amino group and the strongly electron withdrawing 3-cyano group. Since metal-ligand π-bonding would be facilitated by electron withdrawing groups, these results support the fact that the sign of the last term in equation (3) is positive in pyridine complexes. νC=O is lowered by 15 cm^{-1} between the extremes of electron release and electron withdrawal. That νC=O is lowered by electron withdrawing substituents is in agreement

with the observed effect of similar substituents in the series of complexes $Ni(ACA)_2(R\text{-}C_5H_4N)_2$ to be discussed in a later section.

NAKAMOTO and colleagues[109] in a study of various $UO_2(ACA)_2$ solvates have attempted to assign νU-O by comparison with their normal coordinate treatment of $Cu(ACA)_2$.[78] A peak occurring at round 404 cm^{-1} was assigned as an out-of-plane bending mode whilst a very low intensity, high frequency shoulder of this peak was assigned to νU-O. The IR spectra of the twenty-six substituted pyridine adducts of $UO_2(ACA)_2$ prepared in this section displayed a peak around 404 cm^{-1}, the high frequency shoulder seldom being present. On this basis the peak at around 404 cm^{-1} is assigned to a νU-O mode. Whilst no appreciable shift of this peak was observed for electron withdrawing substituents, it is shifted to 413 cm^{-1} for strongly electron releasing substituents. This is in accordance with the previous postulation that electron release by the substituent will reduce the possibility of U-N π-bonding.

In the same study on uranyl complexes,[109] NAKAMOTO and colleagues assign a peak occurring at 627 cm^{-1} in $UO_2(ACA)_2 \cdot py$ as (νU-O + $\delta C\text{-}CH_3$). Since this peak manifests itself in all complexes of pyridine including the seven pyridine adducts of uranyl β-ketoenolates and the five pyridine adducts of uranyl *o*-hydroxyarylcarbonyl complexes discussed in this section, $VO(ACA)_2 \cdot py$,[109] $Ni(ACA)_2(py)_2$[109] and forty complexes of pyridine of the type MX_2py_2, MX_2py_3 and MX_2py_4 (M = Zn, Hg, Co, Cu, Mn, Ni, Cr, Cd, Fe, Pb, Ca; X = Cl, Br, I, NCS, NO_3),[119-120] it would appear that this band is due to the pyridine molecule and is derived from the peak occurring at 602 cm^{-1} in free pyridine.[121]

The same communication[109] also contains the incorrect assignments of νC=O and νC=C (see Introduction). It would appear, therefore, that whilst normal coordinate treatments of complex molecules may be considered useful as a guide to the assignment of IR active modes, the results produced must not be too rigorously applied to the observed spectrum. It is suggested here that a compromise between normal coordinate treatments and empirical assignments using a large series of structurally and compositionally similar compounds may be the best approach to assigning IR active modes of complex molecules.

The effect of the pyridine substituent on νU=O in the complexes $UO_2(ACA)_2 \cdot R\text{-}C_5H_4N$ was verified by the preparation of series of substituted pyridine adducts of $UO_2(TFA)_2$, $UO_2(DPM)_2$, $UO_2(BZA)_2$ and $UO_2(DBM)_2$. In all cases it was found that electron release by the substituent caused a shift of νU=O to lower wavenumbers, with the exception of the benzoylacetonate complexes. In the latter class of complexes, U-N π-bonding cannot play an important role in the mode of adduction.

The NMR spectra (Figs. 20-21) of the compounds discussed so far in this section support the results found in the IR study. For the series of complexes of the type $UO_2(\beta\text{-diketone})_2 \cdot py$ it was found that the chemical shift of the 2(6)-protons of the pyridine molecule follow the same order as U=O on changing the chelate ring substituent, increased U=O bond strength causing shielding of the protons. This would be expected since the 2(6)-protons lie close to the sphere of influence of the C=O and U=O bonds. It was also found that the 4-proton of the

pyridine molecule is deshielded with increased U=O bond strength. The 4-proton is far removed from any influence of the β-ketoenolate ring (except the electronic effect of the substituent). A similar situation obtains for the pyridine N-oxide adducts of uranyl β-ketoenolates.

Of the twenty-six substituted pyridine adducts of $UO_2(ACA)_2$ prepared in this section, only twelve were soluble in deuterochloroform. The NMR spectra of these complexes indicate no discernable trend of the chemical shift of the pyridine ring protons with the σ values of the substituent. (Such a trend was found for the free pyridines - see section (8) of Discussion). This is in accordance with the postulation that U-N π-bonding is of importance in these compounds.

Magnetic susceptibilities of uranyl complexes prepared in this and the preceeding sections indicate that the complexes are weakly diamagnetic, giving values of μ eff. of the order of +0·01 BM. There is thus no major difference between the magnetic properties of the uranyl ion in these compounds.

4. VANADYL β-KETOENOLATES

The vanadyl moiety in coordination complexes has been extensively studied. Experimental evidence for the existence of the vanadyl ion, VO^{++}, in aqueous solution is strong, although not unambiguous.[122-124] X-ray diffraction studies of the complexes $VOSO_4 \cdot 5H_2O$[125] and $VO(ACA)_2$[59] clearly demonstrate the existence and stability of the VO^{++} entity in solid complexes. It has been found that even in VO_2, which crystallizes in a highly distorted rutile structure, there is one short V-O bond in each VO_6 unit.[126] Chemical analysis and molecular weight determinations have established that the formula of vanadyl acetylacetonate is $VO(ACA)_2$ and that it is monomeric in benzene solution.[58]

Indirect evidence for the mononuclear monoxy VO^{++} species may be deduced from the IR spectra of vanadyl complexes. BARRACLOUGH and colleagues[65] examined the IR spectra of several complexes which contained metal-oxygen multiple bonds, and reported that $\nu M{=}O$ generally occurs in the range 1100-900 cm^{-1}. Specifically they reported V=O stretching frequencies at 1020 cm^{-1} for $VOSO_4$, 995 cm^{-1} for $VO(ACA)_2$, 976 cm^{-1} for a complex vanadyl oxinate and 967 cm^{-1} for a complex vanadyl malonate. Vanadium(IV) hydroxide has been formulated as $VO(OH)_2$ on the basis of its IR spectrum[64] which shows a strong V=O stretching frequency at 955 cm^{-1}. It is apparent from the above values for band maxima that the environment of the VO^{++} entity conditions a marked effect upon the stretching frequency and hence upon the force constant and strength of the V=O bond. This is not unexpected, since McGLYNN and colleagues[115] have shown that the magnitude of $\nu U{=}O$ asym. may be used as a probe to establish a ligand series exhibiting a parallel with the spectrochemical

The persistence of the oxovanadium(IV) species in a number of compounds makes possible the utilization of the properties of the oxycation species in a study of the bonding and structure of this d^1 electron system. Thus $\nu V{=}O$ should serve as a sensitive probe, as in the case of uranyl complexes, from which certain structural and bonding features of the molecule as a whole may be deduced.

The vanadium atom in vanadyl complexes may be either five or six coordinate. Microanalyses, molecular weight determinations and conductance data will generally suffice to settle this point.[127] The electronic energy levels in the vanadyl entity and its complexes quoted in the following discussion have been deduced from the molecular orbital scheme of BALLHAUSEN and GRAY.[124]

The V=O bond in vanadyl complexes is a multiple covalent bond consisting of $p\pi \rightarrow d\pi$ donation of electrons by the oxygen to the vanadium, superimposed upon the σ-bond. The amount of $p\pi \rightarrow d\pi$ donation depends both on the capacity of oxygen to donate and vanadium to accept electrons. The donating tendency of the oxygen atom, which may be associated with the high electron density in the filled valence level of the small oxygen atom,[128] should be very little affected by the presence of coordinated ligands. The electron accepting capacity of vanadium(IV) on the other hand, which has one half-filled and four empty d orbitals should be markedly affected by coordinated ligands. Coordinated ligands which donate their electron pairs will increase the electron density in the metal d orbitals and consequently the $p\pi \rightarrow d\pi$ donation from oxygen to vanadium is expected to be reduced to an extent which depends upon the donor ability of the ligand. As

a result there will be a lowering of the V=O bond order and hence νV=O. The amount of metal-ligand π-bonding is expected to be small as there is only one d electron present in the VO^{++} system. Consequently both σ- and π-ligand-to-metal bonding must be important.

The above argument can be elegantly demonstrated by a comparison of the IR spectra of $VO(ACA)_2$ and $VO(ACA)_2 \cdot py$. On the basis of the above argument it would be expected that on adduction of a pyridine molecule to $VO(ACA)_2$, νV=O would decrease. This is observed, the decrease being from 999 to 973 cm^{-1}. Also expected would be a decrease of νV-O and all bands assigned as V-O modes (whether coupled or not) do show a decrease, the largest observed shift being for the band at 488 cm^{-1} in $VO(ACA)_2$ which is lowered to 465 cm^{-1} in the pyridine adduct. νC=O is increased from 1564 cm^{-1} in the unadducted molecule to 1586 cm^{-1}.

For the first part of this study seven variously-substituted β-ketoenolate complexes of the type $VO(L)_2$ were prepared with the object of observing any changes in νV=O caused by the chelate ring substituents. Fig. 31 shows νC=C, νC=O, νV=O and the two V-O modes plotted against an arbitrary order of the ligands. The slight shift of νC=C with change of chelate substituent indicates that the strength of this bond remains more or less constant throughout the series. It is apparent from Fig. 31 that there is an inverse relationship between νV=O (and νV-O) and νC=O, *i.e.*, as the strength of the C=O bond increases, so the strengths of the V=O and V-O bonds decrease. Plots of νC=O against νV=O and νV-O (Figs. 32-33) indicate that the situation is somewhat more complicated

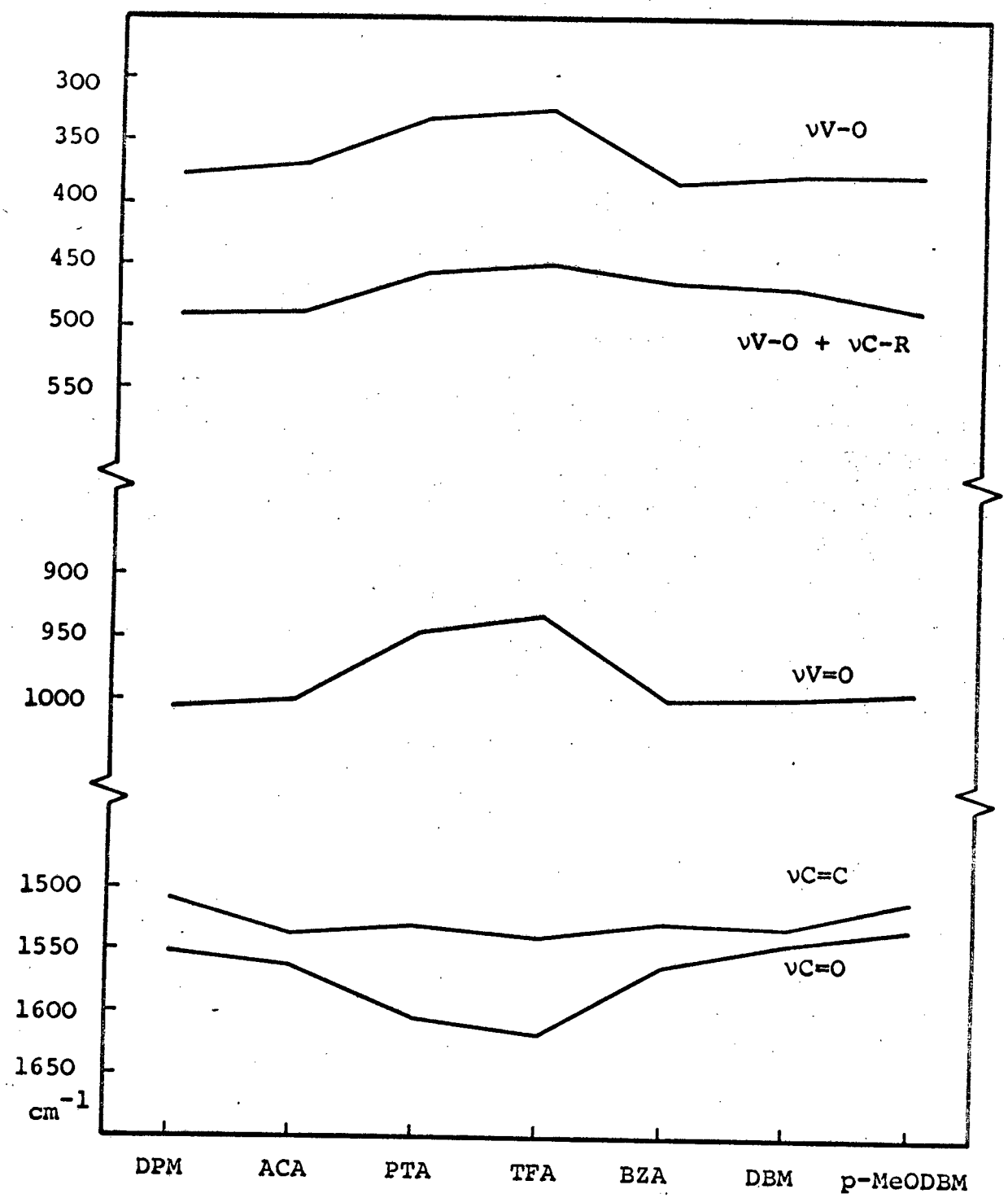


Fig. 31.

Relationship between ligand and various IR stretching modes of the complexes $VO(L)_2$.

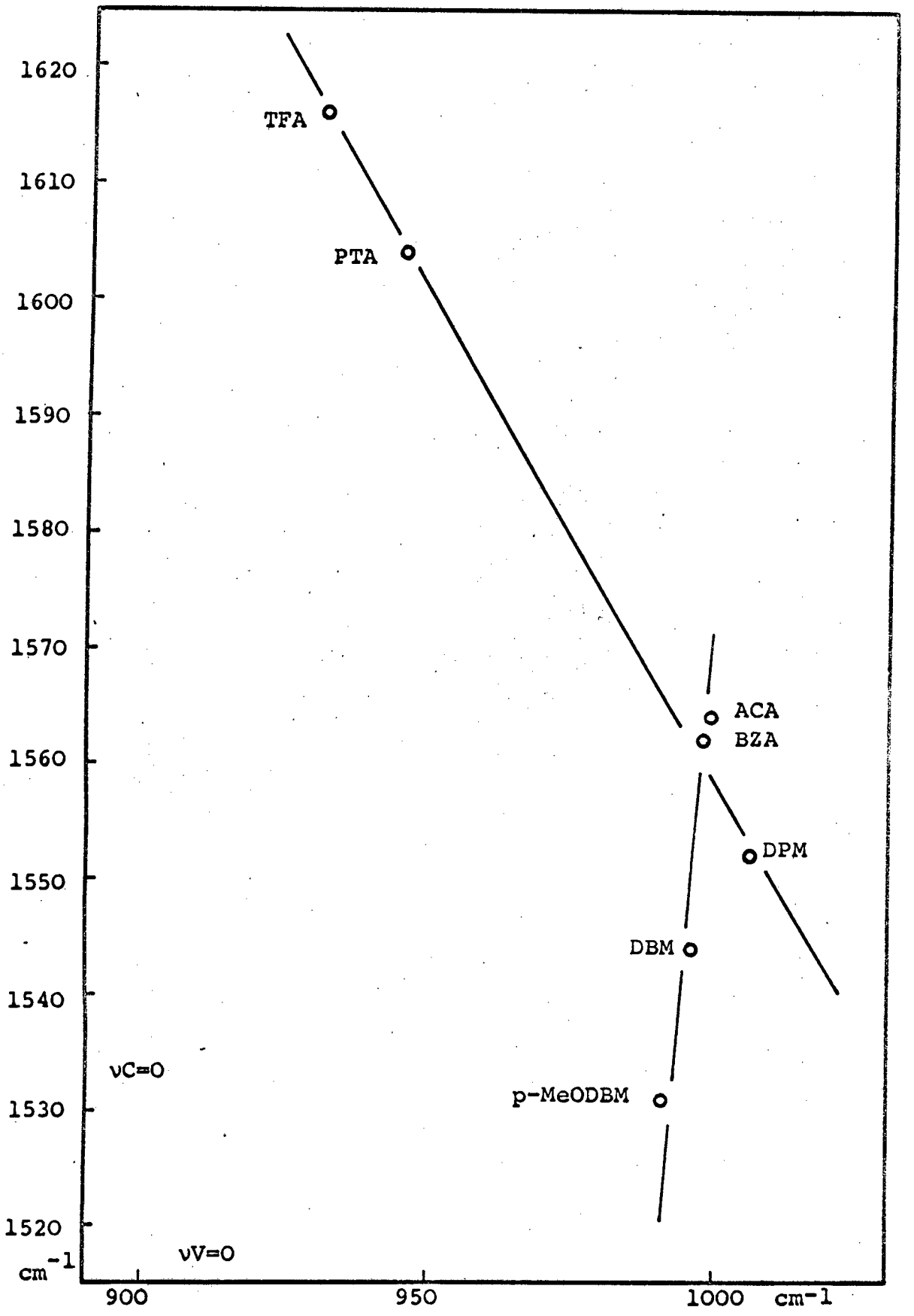


Fig. 32.

Relationship between νC=O and νV=O for the complexes $VO(L)_2$.

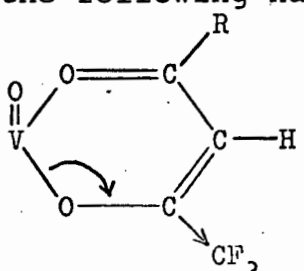
than would at first be anticipated. It is clear from Figs. 32-33 that two alternate situations obtain depending upon the nature of the chelate ring substituent. Phenyl substituents cause only a small shift of $\nu V{=}O$ and the lower frequency $\nu V{-}O$ band but induce a fairly large shift of the higher frequency coupled $\nu V{-}O$ band. This may imply the necessity for revised assignments of $\nu V{-}O$. The band of lower frequency could well be coupled $\nu V{=}O$ since the shift of this band parallels that exhibited by the "pure" $\nu V{=}O$ band. Figs. 32-33 indicate that the vanadyl β-ketoenolates can be separated into two distinct classes, those derived from HTFA, HPTA, HACA and HDPM, and those derived from HBZA, HDBM and p-MeODBM.

Amongst the vanadyl complexes of the former class, $VO(TFA)_2$ exhibits the strongest C=O bond, the weakest V=O bond and the weakest V-O bond. The pronounced electron withdrawing effect of the CF_3 groups causes HTFA to be strongly acidic, thus raising the donor capacity of the oxygen atoms. This leads to increased electron density in the d orbitals of the vanadium atom, reducing the amount of $p\pi \rightarrow d\pi$ donation from the multiply bonded oxygen atom. This leads to a reduction in strength of the V=O bond as observed by the shift of $\nu V{=}O$ to lower wavenumber. This is the precise opposite of the situation obtaining in uranyl complexes, where electron withdrawal by the chelate ring substituent was found to shift $\nu U{=}O$ to higher wavenumber. It was found by McGLYNN and colleagues[115] (as discussed in the previous section) that the decrease in $\nu U{=}O$ is given by:

$$\Delta\nu = -\text{electrostatic effect} - \sigma(L\rightarrow M) - \pi(L\rightarrow M) \pm \pi(M\rightarrow L)$$

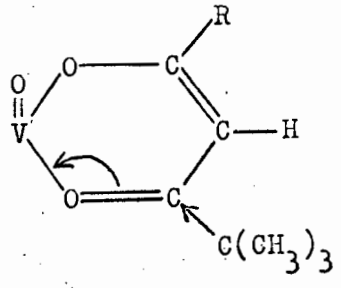
In vanadyl complexes the last term of this equation will be of little, if any, importance since there is only one 3d electron available for metal-ligand π-bonding, whereas in uranyl complexes there are ten 5d electrons capable of taking part in metal-ligand π-bonding, indicating that the last term in the equation could be of great importance. If it is assumed that the first three terms in the equation have similar sign and magnitude in the uranyl and vanadyl series (as seems likely) then the direction and magnitude of shift of νM=O will hinge on the sign and relative significance of the final term. McGLYNN and colleagues inferred that V-O π-bonding is negligible in the vanadyl series but of importance in the uranyl series and induces opposed sign of Δν.

The inverse relationships exhibited between the strengths of the V-O and C=O bonds can be explained assuming electronic shifts of the following nature to occur



due to the inductive effect of the CF_3 group. Vanadium(IV) has only one d electron, hence stabilization of the V-O bond by metal-ligand π-bonding will occur to a small extent only. The complex at the other extreme of this class is $VO(DPM)_2$. In this complex the strength of the C=O bond decreases as the V=O and V-O bond strengths increase, relative to $VO(TFA)_2$. The tertiary butyl ring substituents in $VO(DPM)_2$ are strongly electron releasing, thus reducing the donor capacity of the oxygen atoms. This results in high νV=O and consequently a

strengthening of the V=O bond. The increase in strength of the V=O bond with decreasing C=O bond strength can be explained if electronic shifts of the following nature occur



due to the electron releasing effect of the tertiary butyl group. Here again there will be little additional stabilization of the complex due to metal-ligand π-bonding.

A vanadyl complex of tropolone (HT) has been described[129] and formulated $VO(T)_2$ on the basis of elemental microanalytical results. This complex displays νV=O at 984 cm^{-1}. Since HT is known to be a stronger acid than HACA[130] this value for νV=O is in accordance with the previously discussed results. It is of interest to note that the vanadyl complex of hexafluoroacetylacetone has been prepared.[63] It has been shown by elemental microanalysis and IR investigations that this complex exists as the monohydrate $VO(HFA)_2 \cdot H_2O$. If this complex was anhydrous νV=O would be expected to be lower than that reported for $VO(TFA)_2$ at 931 cm^{-1}, however νV=O occurs at 944 cm^{-1}. This increase must be due to either the increase in coordination number, the change in structure of the complex or the effect of the coordinated water molecule.

Figures 32-33 indicate that phenyl substituted vanadyl β-ketoenolates behave in a completely different manner to the β-ketoenolates discussed above. The order of these ligands in

in terms of increasing carbonyl frequency is HBZA > HDBM > Hp-MeODBM. The shift of νC=O between the two extremes is 31 cm^{-1}, whereas νV=O and the lower frequency νV-O show a shift of 7 cm^{-1} over the same range of compounds. The higher frequency νV-O displays a large shift (23 cm^{-1}) over the same range of compounds. Phenyl substitution of the β-ketoenolate ring leads to an increase in the resonance possibilities of the complex, resulting in a certain amount of pseudo-aromaticity of the chelate ring. This has a stabilizing effect on the complex as a whole. It is clear that the increased possibility of quinonoid resonance will confer extra stability upon the C=C and V-O bonds at the expense of the C=O bond, as is observed in practice. It is also apparent that on changing the substituent from one phenyl group to two phenyl groups to two *p*-methoxyphenyl groups the quinonoid resonance form will be favoured, *p*-methoxyphenyl groups favouring this form most of all as the methoxy group is strongly electron releasing. The V=O bond would not be expected to show much change with phenyl substituted β-ketoenolates since their effects are concentrated mainly in the chelate ring.

On the basis of the above discussion it would appear that the assignment of the band around 350 cm^{-1} as $\nu V\text{-}O^{109}$ in vanadyl β-ketoenolates should be revised, since the shifts on change of the chelate ring substituent parallel those observed for νV=O near 980 cm^{-1}. It is suggested here that the band near 350 cm^{-1} is probably a coupled νV=O mode. In all the vanadyl β-ketoenolates studied in this work it can be seen that the effect of the chelate ring substituent is transmitted through the vanadium atom to the V=O bond. The order of ranking

of the β-ketoenolates according to the strength of the V=O bond is HDPM > HACA ~ HBZA ~ HDBM ~ Hp-MeODBM >> HPTA > HTFA. This order is found to be consistent with the order of the $\Sigma\sigma$ values derived from the *F* and *R* values of SWAIN and LUPTON[117] discussed in the previous section, with slight deviation of the νV=O values for $VO(BZA)_2$ and $VO(DBM)_2$.

L	TFA	PTA	DBM	BZA	ACA	DPM	
$\Sigma\sigma$	+0.45	+0.31	-0.18	-0.16	-0.15	-0.22	
νV=O	931	945	996	998	999	1006	cm^{-1}

This implies that the weightings of f and r should be altered slightly in this series of complexes.

X-ray diffraction studies on $VO(ACA)_2$[59], $VO(BZA)_2$[131] and $VO(DBM)_2$[132] indicate that these compounds are isostructural, consisting of discrete molecules in which the five oxygen neighbours of vanadium are at the corners of a rectangular (nearly square) based pyramid, with the vanadium approximately at its centre of gravity. The V=O bond is considerably shorter than the V-O bonds. For the purposes of the preceeding discussion it has been assumed that the vanadyl β-ketoenolates are all isostructural. This is not unreasonable since magnetic susceptibility measurements on all the compounds prepared in this section indicate an average value of μ eff. of 1.72 BM. This is good evidence that these complexes exist as discrete molecules since polymerization by metal-metal bonding would invoke spin-pairing of the d electrons and a consequent reduction in the value of μ eff.

Having studied the effect of changing the chelate ring substituent, it was considered to be of interest to study the

effect of changing a substituent exocyclic to the β-ketoenolate ring. A series of adducts of $VO(ACA)_2$ with variously substituted pyridines was prepared and their IR spectra determined. It has previously been demonstrated that $VO(ACA)_2$ forms mono adducts of the type $VO(ACA)_2 \cdot B$ with various donor ligands.[58] GARVEY and RAGSDALE[60] determined the solution IR spectra of a series of 4-substituted pyridine N-oxide adducts of $VO(ACA)_2$, $VO(TFA)_2$ and $VO(BZA)_2$. The linear relationship between $\nu V{=}O$ and $\bar{\sigma}$ (substituent parameters derived specifically for pyridine N-oxides[133]) for the adducts of $VO(ACA)_2$ and $VO(BZA)_2$ indicated a decrease in V=O bond strength with increasing donor capacity of the substituent. This would be expected since increased electron donation by the substituent reduces the amount of $p\pi \rightarrow d\pi$ donation possible from the vanadyl oxygen to the vanadium atom. For the series of pyridine N-oxide adducts of $VO(TFA)_2$ no change in the strength of the V=O bond was apparent with change of substituent. This was explained by the authors as being due to the "electronic distortions" introduced by the fluorine atoms. It is suggested here that any effect due to the adducted pyridine N-oxide will be overcome by the strongly electron withdrawing capacity of the highly inductive CF_3 groups. This is demonstrated by the fact that on adduction $\nu V{=}O$ is lowered by only 3 cm^{-1} in these complexes. In the case of the pyridine N-oxide complexes of $VO(ACA)_2$ the situation is reversed. The CH_3 groups have an electron donating effect, thus the donor effect of the adducted molecule cannot be transmitted through the vanadium atom to the chelate ring, and must be felt on the V=O bond by reducing the amount of $p\pi \rightarrow d\pi$ donation to the

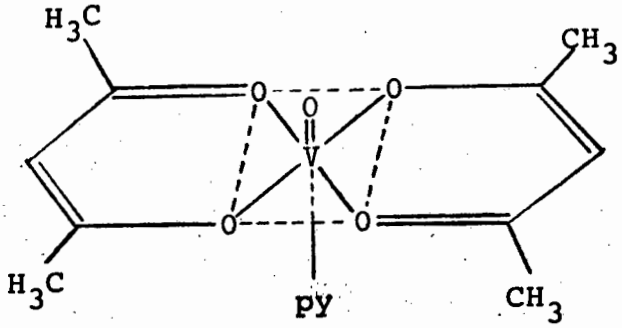
vanadium atom. $\nu V{=}O$ of the adduct displays a lowering of 30-50 cm^{-1} from $VO(ACA)_2$, depending upon the nature of the substituent.

It was considered of interest to observe whether the series of substituted pyridine adducts of $VO(ACA)_2$ prepared in this work would show similar results to the pyridine N-oxide adducts discussed above. Fourteen variously substituted pyridine adducts of $VO(ACA)_2$ were prepared. For nine of these complexes $\nu V{=}O$ was lowered by 42 ± 4 cm^{-1} and for five of the complexes $\nu V{=}O$ was lowered by 29 ± 4 cm^{-1}. In the former class of compounds $\nu V{=}O$ showed no dependance upon the electronic nature of the substituent, whereas it was evident in the latter class of compounds that electron release by the substituent caused a reduction in $\nu V{=}O$. An earlier study[134] yielded a similar result. It was found that the IR spectra of chloroform solutions of $VO(ACA)_2$ and various "strongfield" ligands such as pyridine, ammonia and various primary and secondary aliphatic amines showed a reduction of 48 ± 3 cm^{-1} in $\nu V{=}O$ (it should be noted that $\nu V{=}O$ of $VO(ACA)_2$ occurs at 1004 cm^{-1} in chloroform solution as opposed to 999 cm^{-1} in nujol mull). "Weak field" ligands such as phosphines, arsines, sulphides and thiourea caused no shift of $\nu V{=}O$ and intermediate ligands such as tetrahydrofuran and *p*-dioxane caused an intermediate shift of 23 ± 1 cm^{-1}. These results were not explained but it was observed that the large shifts of $\nu V{=}O$ could not be caused by simple mass effects. Calculation showed that a simple mass effect due to adduction of a molecule of pyridine should lower $\nu V{=}O$ by 6 cm^{-1} whereas the observed shift in nujol mull is 26 cm^{-1}. It therefore appears that while the mass effect is significant in an absolute

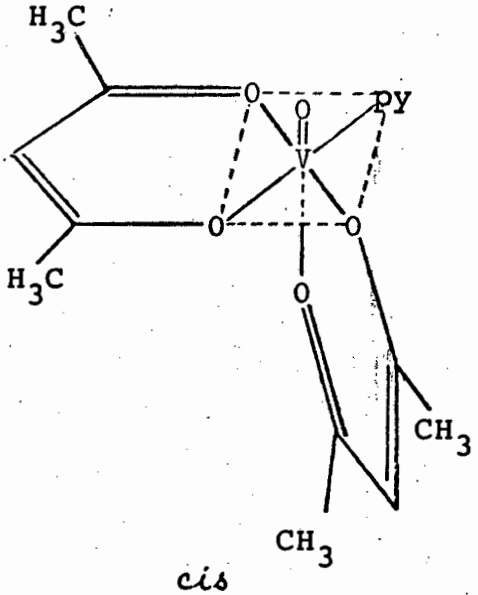
sense, it does not contribute more than about 20% to the magnitude of the observed shift. Most of the substituted pyridines employed in this study have comparable molecular weights, hence mass effects can be considered approximately constant throughout the series. The position of the substituent on the pyridine ring plays no part in determining to which class the adducts belong, as both 3- and 4-substituted pyridines occur in both classes.

In an attempt to resolve the problem of two almost constant shifts of $\nu V{=}O$ in these complexes, the far IR spectra were studied. On coordination of a pyridine molecule to $VO(ACA)_2$ the four V-O modes at 611, 488, 426 and 367 cm^{-1} (with the possible exception of the 367 cm^{-1} band - see previous discussion) are lowered to 601, 465, 422 and 362 cm^{-1}. Simultaneously $\nu C{=}O$ is increased from 1564 cm^{-1} to 1586 cm^{-1}. In the series of five substituted pyridine adducts which showed the smallest reduction in $\nu V{=}O$ the four bands mentioned above all occur at approximately the same frequencies. In the series of nine substituted pyridine adducts which show the larger reduction in $\nu V{=}O$ these same four bands occur at around 588, 456, 413 and 350 cm^{-1} indicating a greater decrease in the stability of these complexes. In this series the bands at 588, 456 and 350 cm^{-1} are split, displaying extra peaks at around 552, 435 and 335 cm^{-1}. This would indicate a reduction in the degree of symmetry of the complexes, which would also explain the additional weakening of the V=O and V-O bonds. It is for this reason that it is suggested here that these compounds exist

as *cis*- and *trans*-geometrical isomers of the following structures



trans



cis

The series of nine complexes which display greatest weakening of the V=O and V-O bonds are probably *cis*-isomers and the series of five complexes which are more stable are probably *trans*-isomers. A *cis* arrangement of the chelate rings is not unlikely and has been verified for the complex $Ni(ACA)_2(pyNO)_2$ and some cobalt(II) complexes of HACA.[135]

Soon after the completion of this work DA SILVA and WOOTTON[61] reported similar results for the solution IR spectra of $VO(ACA)_2$ and a series of substituted pyridines in chloroform. By examination of the shift of $\nu V{=}O$ it was deduced that there is an equilibrium between geometrical isomers in chloroform solution. No far IR spectra were studied, and the final conclusions reached were that the complex in the *trans* form is that with the lowest $\nu V{=}O$ value. After studying the far IR spectra of these compounds the conclusions reached herein, *i.e.* the opposite of those reached by DA SILVA and WOOTTON, are considered to be a more accurate description of the true structures of these isomers. In the note mentioned above[61] it was stated that attempts were in progress to isolate

isomers of the two different types in the solid state. To date this work has not been published.

5. SUBSTITUTED PYRIDINE ADDUCTS OF NICKEL(II) ACETYLACETONATE

Square planar complexes of nickel(II) may undergo an equilibrium with additional ligands in the following manner

$$NiL_4 + 2B \rightleftarrows NiL_4B_2$$

If the additional ligand B is a good donor, then in many cases the equilibrium will lie far to the right, resulting in an isolable octahedral complex. Examples of such ligands are water and nitrogenous bases such as pyridines and amines. Thus it would be expected that if $Ni(ACA)_2$ had monomeric square planar structure, bis(pyridine) adducts of the form $Ni(ACA)_2(py)_2$ could be isolated. X-ray crystallographic studies indicate that the molecule exists as a trimer,[136] some oxygen atoms of the HACA molecule being shared between two nickel atoms, resulting in each nickel ion attaining octahedral configuration. While it is known[66,71] that trimeric anhydrous $Ni(ACA)_2$ reacts with water and nitrogenous bases to form monomeric octahedral bis adducts, displacement of water from the dihydrate by a substituted pyridine provides a more convenient synthesis.

Contrary to the behaviour of HACA, certain other β-diketones do form square planar complexes with nickel(II). The complex $Ni(DPM)_2$ is anhydrous, monomeric and square planar[137] as a result of the steric repulsion imposed upon the molecule by the bulky tertiary butyl groups. The pink $Ni(DPM)_2$ complex is diamagnetic, but in the presence of water or nitrogenous bases the green paramagnetic bis adduct is formed.

The higher ligand field strength of the pyridine

molecule causes a general colour change from green $Ni(ACA)_2(H_2O)_2$ to blue $Ni(ACA)_2(py)_2$. *Trans* octahedral configuration has been established for several base adducts both by X-ray structural[71,138] and spectrophotometric[71] methods. *Cis* complexes have been described, *e.g.* the bis(pyridine N-oxide)[135] and 2,2'-bipyridine[139] adducts of $Ni(ACA)_2$. The internal similarity of the IR spectra (Fig. 17) of all compounds prepared in this section suggests that they all have *trans* configuration. Magnetic susceptibilities of complexes $Ni(ACA)_2(R\text{-}C_5H_4N)_2$ prepared in this section display average values of μ eff. of 3·1 BM.

R	μ eff.(BM)
3,5-di-Cl	3·10
4-$COCH_3$	3·09
H	3·11
3,4-di-CH_3	3·10
4-$N(CH_3)_2$	3·10

This is additional evidence for a mononuclear species, indicating the absence of polymerization by the formation of Ni-Ni bonds. That the Ni-N bond is weak is indicated by the absence of any band in the far IR region which may be ascribed to a Ni-N mode. Since even the comparatively strongly bound pyridine in $NiCl_2py_2$ yields[140] a frequency of 239 cm^{-1} for νNi-N, this vibration almost certainly lies below 200 cm^{-1} in the adducts. Despite the weak bonding of the pyridines, bis adducts are always obtained.

Assignment of νNi-O in the IR spectrum of $Ni(ACA)_2$ has been subject to some confusion (see Introduction). On the basis of a normal coordinate treatment[78] of $Cu(ACA)_2$ and its subsequent extension[109] to the corresponding nickel(II)

complex, a band at 452 cm^{-1} was assigned as νNi-O. This conclusion is subject to some doubt, since the theoretical treatment assumes square planar stereochemistry, while subsequent work [136] has shown that the complex has trinuclear octahedral structure. Furthermore, the composition of the compound was not specified in earlier reports. Thus one report[141] lists the higher frequency νNi-O at 569 cm^{-1}, another[142] as a doublet of mean frequency 529 cm^{-1}. It has been found in this work that the analytically pure dihydrate absorbs at 570 cm^{-1} and the anhydrous complex at 593 cm^{-1}. It seems clear that the earlier reports refer to these alternative species. The most convincing assignments arise from ^{18}O-labelling studies[83] which show that two specific bands in the far IR region are appreciably shifted by insertion of the heavier isotope and are therefore likely to represent M-O stretching modes. When a comparison of the spectra of the adducts with those of the acetylacetonates of nickel(II) and other metal(II) ions is made these two bands are readily identified. Furthermore, only these two bands in the far IR region are sensitive to change of substituent of the adducted pyridines. These results therefore support the assignments based on ^{18}O-labelling studies.

It has been found that in a series of metal β-ketoenolates the chelate ring substituent has an influence on the C=O and M-O bond strengths (*e.g.* see section on vanadyl complexes). Complexes with electron releasing chelate ring substituents were found to have low C=O and high M-O bond strengths compared with those possessing electron withdrawing substituents. This was explained on the basis of the inductive effect of an electron withdrawing group causing an electronic

shift from the M-O to the C=O bond, and an electron releasing group causing the reverse shift. In the series of variously substituted pyridine adducts of $Ni(ACA)_2$ examined in this section, the change of substituent is exocyclic to the chelate ring.

The gross effect of adduct formation is to lower the value of νNi-O found for the parent anhydrous complex. The decrease is evidently associated largely with change of composition rather than coordination number, since the anhydrous complex, the dihydrate and the bis(pyridine) adducts all have octahedral structure. That the combined shifts of both the νNi-O bands is greater on pyridine adduct formation than on hydration may be attributed to the higher ligand field strengths of pyridines, since they lie to the right of water in the spectrochemical series. A further increase in ligand field strength is expected to accompany the introduction of electron releasing substituents in the coordinated pyridines. This arises from enhancement of the donor capacity of the lone pair of electrons of the nitrogen atom of the pyridine ring and hence increased metal-pyridine interaction. As an index of the electronic effects of the substituents, the HAMMETT σ values[5] are employed. These values have been shown to apply with satisfactory precision to pyridine substituents also.[6]

Fig. 34 shows the correlation between the two Ni-O modes and the substituent constants of the substituted pyridines. The linear relationship displayed indicates that electron releasing substituents lower the Ni-O frequencies and hence bond strengths, while electron withdrawing substituents have the

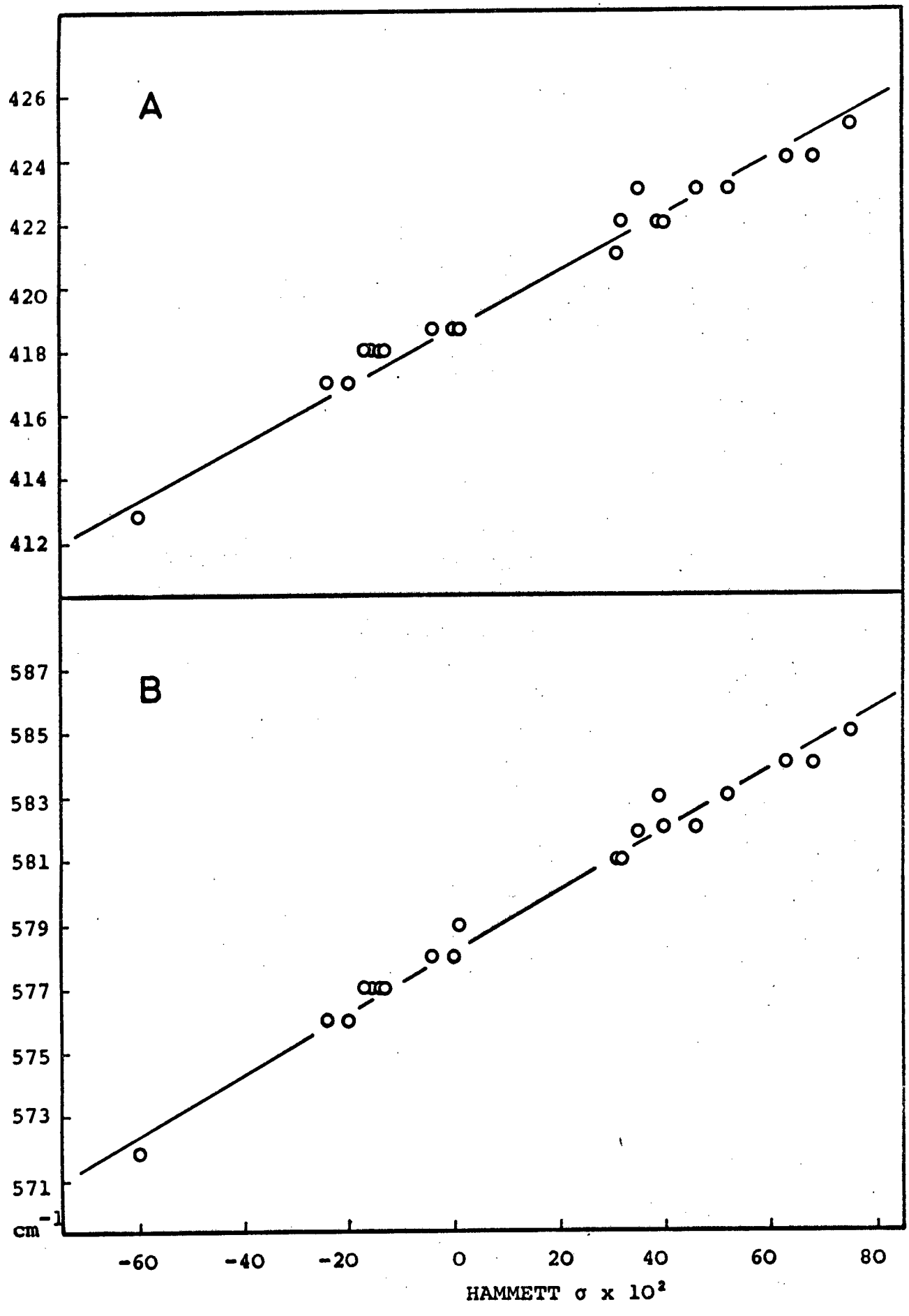


Fig. 34.

Relationship between σ and A; νNi-O + νC-CH_3,

reverse effect, relative to the unsubstituted pyridine adduct. These trends can be explained on the basis of the electronic effects existing in the molecule, as detailed earlier. The CH_3 groups of the chelate ring are electron releasing and tend to produce an electronic shift from the C=O to the Ni-O bond. The electron releasing substituents of the coordinated pyridines will tend to oppose this electronic effect, assuming the electron drift from the pyridine to be transmitted through the metal atom. This will cause the Ni-O bond strength, and thus the frequencies of the Ni-O modes to be lowered relative to the unsubstituted pyridine adduct. This is not an obvious result of introducing electron releasing substituents since if the electronic effect were transmitted to the Ni-O bonds by substituent-aided metal-ligand π-bonding, an increase in the Ni-O bond strength would be expected. The latter mechanism is apparently not significant in determining the Ni-O bonding. Electron withdrawing substituents tend to promote the electron releasing effect of the CH_3 groups of the chelate ring giving rise to higher νNi-O, consequently stronger Ni-O bonds relative to the unsubstituted pyridine adduct.

In support of the assumption that the electronic effects are transmitted through the nickel ion, it has been found[89] that nickel(II) hexafluoroacetylacetonate exists solely as the dihydrate. It would therefore appear that the strongly electron withdrawing character of the chelate ring substituent is transmitted through the metal ion, promoting adduction to such an extent that adducted molecules cannot easily be removed.

A secondary effect of varying the pyridine substituent is the increase in strength of the C=O bond accompanying the introduction of electron releasing pyridine substituents.

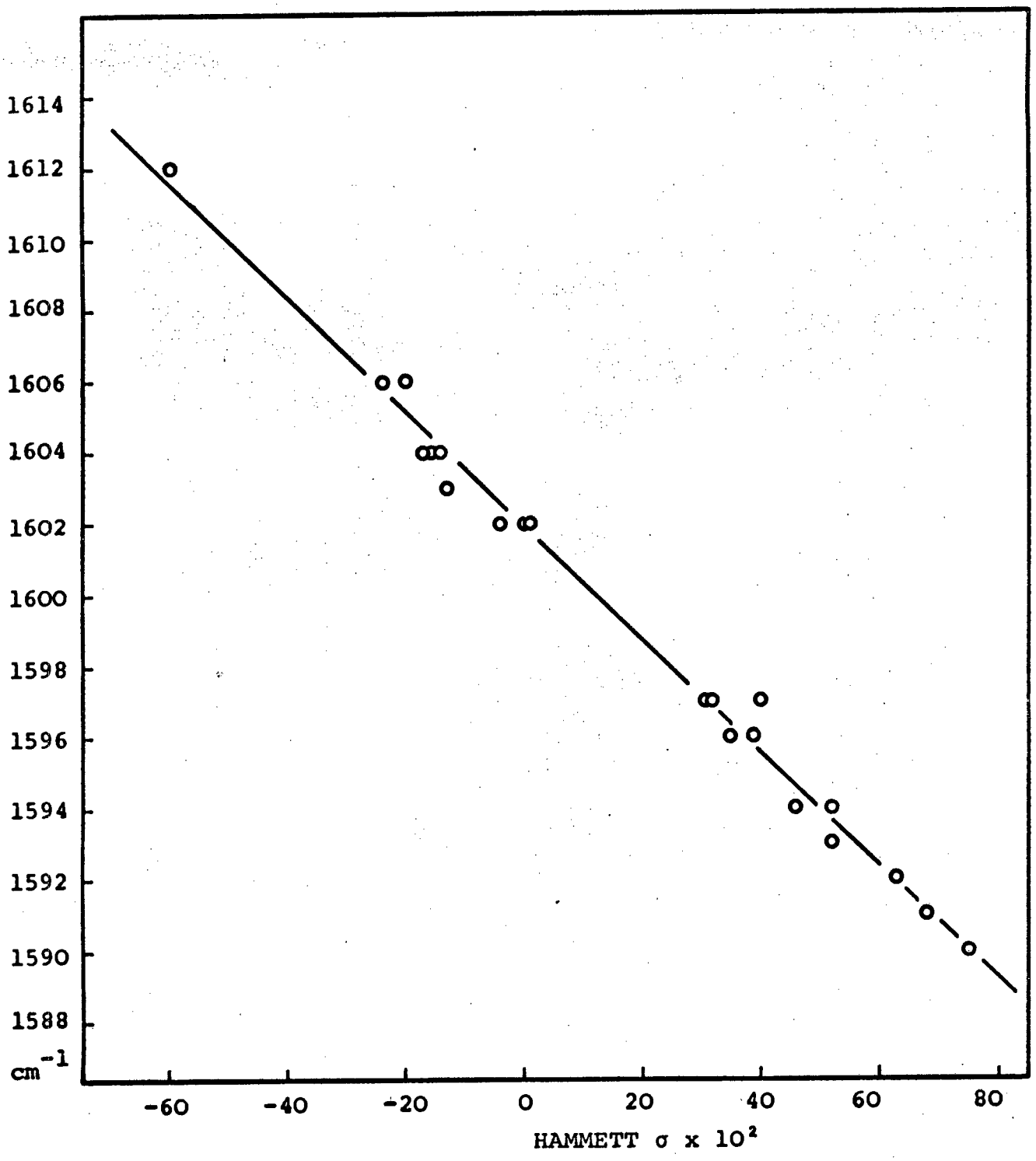
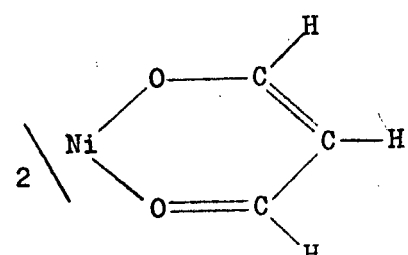


Fig. 35.

Relationship between σ and νC=O for the complexes $Ni(ACA)_2(R\text{-}C_5H_4N)_2$.

upon the molecule is due to metal-ligand π-bonding. It has been previously demonstrated that metal-ligand π-bonding is not significant in determining the Ni-O bonding, however electron withdrawal by the substituent could cause additional stabilization due to Ni-N π-bonding. Since νNi-N is outside the range of the IR spectrophotometer used in this study, no conclusions can be drawn. If the full-time availability of a UV spectrophotometer was made to this Department, a study of the π - π* transitions in these complexes could be made which should shed some light on the problem.

It is of interest to speculate what would happen if the same series of adducts were prepared of a different β-ketoenolate system, *e.g.* $Ni(TFA)_2$. In the acetylacetonates discussed above, the CH_3 groups have a relatively low electron releasing capacity compared with the very high electron withdrawing capacity of the CF_3 group in $Ni(TFA)_2$. It would be expected that the electronic shifts in the chelate ring would be little affected by the relatively small effect of the pyridine substituent, thus the overall change in the strength of the Ni-O and C=O bonds would not be as large as in the case of the acetylacetonates. Similarly, in a series of $Ni(DPM)_2$ adducts of the same pyridines it would be expected that the overall change in the Ni-O and C=O bond strengths would be smaller than the overall change in the acetylacetonates, as the electronic drift from the C=O to the Ni-O bond will be enhanced, the effect of the pyridine substituent remaining unchanged. Nickel(II) β-ketoenolates of the following kind



analogous nickel(II) complexes. The anhydrous compounds are very sensitive to aerial oxidation. Anhydrous $Co(ACA)_2$ is trimeric in benzene[69] and triphenylmethane.[145] X-ray diffraction studies[146] indicate that the solid contains tetrameric molecules in which the cobalt atoms have approximately octahedral environments, the linear tetramer being built up by edge-sharing of two pairs of face-sharing octahedra. By contrast it has been found that $Co(DPM)_2$ is monomeric and tetrahedral in structure.[147] In addition to the dihydrate of $Co(ACA)_2$, $Co_2(ACA)_4(H_2O)_2$[148] and $Co_3(ACA)_6(H_2O)$[149] have been identified by X-ray crystallographic methods. In the former compound two octahedra share edges, whereas in the latter, one of the terminal $Co(ACA)_2$ units of $Co_4(ACA)_8$ is replaced by H_2O.

The end product of the reaction of bases with cobalt(II) β-ketoenolates is normally the bis adduct, although in a few cases compounds have been isolated containing more base. $Co(DBM)_2$ for example crystallizes from 4-methylpyridine as an adduct of the type $Co(DBM)_2(B)_4$.[70] The reflectance spectra of these apparently 8-coordinate compounds are similar to those of the 6-coordinate adducts, and it seems likely that the additional base molecules are accommodated in the crystal lattice rather than being coordinated to the metal atom. Crystal structure determinations have shown that the compounds $Co(ACA)_2(H_2O)_2$[150] and $Co(ACA)_2(py)_2$[72] form *trans* octahedral molecules. The two different metal-ligand distances in these compounds suggest that distortion from octahedral symmetry occurs to a greater extent than could be expected from the non-identity of the six donor atoms.

	M-O	M-B
$Co(ACA)_2(H_2O)_2$	2·05	2·23
$Co(ACA)_2(py)_2$	2·03	2·19

Distances in Angstrom units.

IRVING and colleagues[29-30] have established that substituent parameters derived for purely organic systems may be employed to provide useful information on the mode of metal-ligand bonding in metal complexes containing variously substituted organic ligands. Since the metal-ligand stretching frequencies of a series of complexes which differ only in the nature of the ligand substituent are expected (see previous section), in the absence of significant mass effects, to provide a measure of the relative metal-ligand bond strengths, a study of substituent effects in a series of primary aliphatic amine adducts of $Co(ACA)_2$ has been undertaken. The complexes prepared were found to be solely bis(amine) adducts on the basis of elemental microanalytical results and the internal similarities of their IR spectra. Magnetic susceptibility measurements of the complexes $Co(ACA)_2(RNH_2)_2$ showed an average value of μ eff. of 4·83 BM.

R	μ eff. (BM)
H	4·89
C_2H_5	4·75
$i\text{-}C_4H_9$	4·79
$s\text{-}C_4H_9$	4·77

It is evident that polymerization by the formation of Co-Co bonds does not occur in these complexes. The ammonia[139] and cyclohexylamine[74] bis adducts have been previously reported. Although it is known that bis adducts of $Co(ACA)_2$ can be prepared from the anhydrous acetylacetonate,[139] the hydrate is more conveniently employed as a reactant in adduct formation because of its greater stability and higher degree of solubility in the solvents used.

The far IR spectra of the adducts (Fig. 18) reveal that only two bands are substituent sensitive. Comparison of the spectra with that of $Co(ACA)_2(H_2O)_2$ shows that these bands are clearly assigned to νCo-O, the assignments being based on the results of normal coordinate treatments[81-82, 141] and ^{18}O-labelling studies.[83] That no band could reasonably be assigned to a Co-N mode is surprising, since νZn-N has been assigned at 402 cm^{-1} for the complex bis(aniline)zinc(II) chloride.[110,151] This assignment is based on empirical observation[110] and N-deuteration methods.[151] The explanation of the absence of νCo-N may well hinge on the fact that the Co-N bond is very weak compared with the stable Zn-N bond of the zinc complex above, hence νCo-N may be shifted below 200 cm^{-1}, outside the range of the instrument employed in this study. Adduct formation induces a shift of νCo-O of the anhydrous complex to lower wavenumber, as in the case of the substituted pyridine adducts of $Ni(ACA)_2$ (see previous section). This is probably because the higher ligand field strengths of the amines cause firmer bonding to the metal ion than water, and this occurs at the expense of the Co-O bonding in the chelate ring.

For the purpose of examining the substituent dependence of the strength of the Co-O bond, the inductive substituent parameters (σ^*) derived by TAFT[8] are employed as an index of the electronic effects of substituents in non-conjugated systems (where transmission of these effects is by a field mechanism only). The trends observed in the two Co-O stretching frequencies of the bis(amine) adducts of $Co(ACA)_2$ with changing amine substituent are shown in Fig. 36. The basic trends are similar to those observed for the pyridine adducts of $Ni(ACA)_2$. A similar explanation can be employed, except that it would appear that electron withdrawing substituents affect the molecule as a whole more strongly than electron releasing substituents. In this series of complexes it can thus also be demonstrated that the effects of the amine are transmitted through the central metal ion to the chelate ring, the substituent-induced stabilization of the Co-N bond occurring at the expense of the Co-O bonding.

$\nu C{=}O$ of the chelate ring appears as a strong band near 1600 cm^{-1}. Although clearly defined in the spectrum of $Co(ACA)_2$, it is overlaid in the adduct spectra by $\delta N\text{-}H$, and is too broad for its substituent sensitivity to be determined. $\nu N\text{-}H$ exhibits no correlation with σ^*, probably because the proximity of the substituent to the N-H bonds enhances the mass effect. This conclusion is supported by the fact that the band of highest frequency has a maximum value for the substituent of lowest mass (the ammonia adduct). With regard to $\nu N\text{-}H$, it is of interest to note that in a series of substituted aniline adducts of $Ni(ACA)_2$ which have been reported,[73] $\nu N\text{-}H$ shows a correlation with the substituent parameters of the substituted

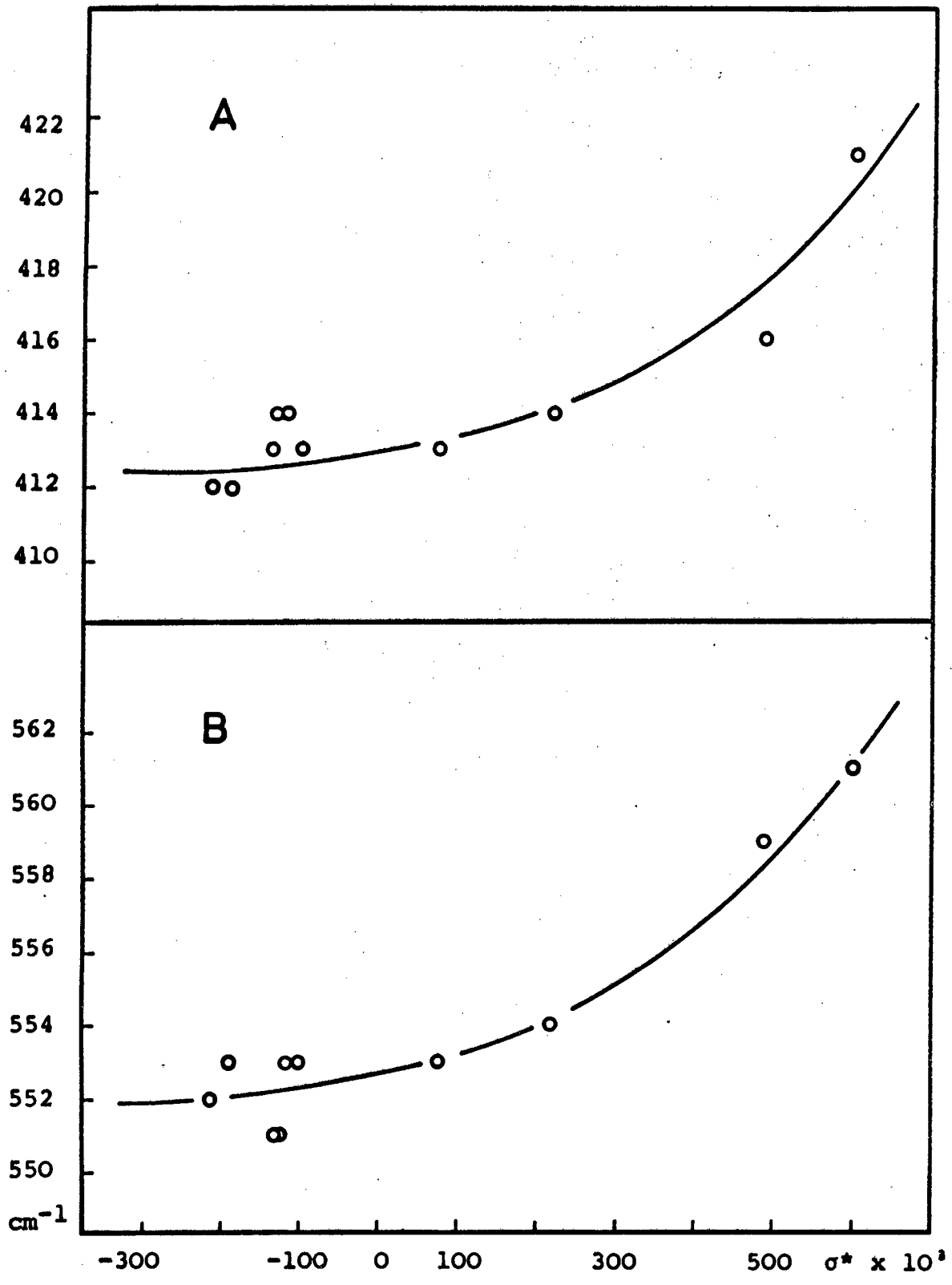


Fig. 36.

Relationship between σ* and A; νCo-O + νC-CH_3
B; νCo-O for the complexes $Co(ACA)_2(RNH_2)_2$.

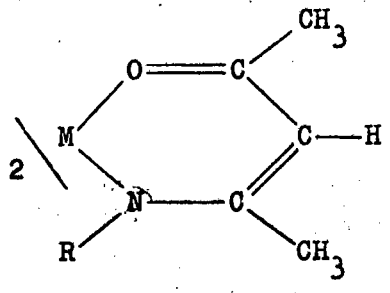
anilines. This is probably due to the fact that the substituent and the NH_2 group are separated by a benzene ring and the mass effect of the substituent will not be as strongly felt by the NH_2 group as when the substituent is directly attached to it.

The results found for the primary aliphatic amine adducts of $Co(ACA)_2$ are similar to those which have been reported[113] for a series of the same adducts of zinc(II) and nickel(II) acetylacetonates. It would appear that similar electronic effects are manifested in all three series. While cobalt(II) and nickel(II) form only bis(amine) adducts, 5-coordination is relatively common amongst the zinc(II) adducts. These differences are undoubtedly associated with the high crystal field stabilization energy of octahedral cobalt(II) and nickel(II), whereas the zero c.f.s.e. of zinc(II) implies that no one stereochemistry is favoured relative to another on the basis of c.f. effects. The amine adducts of zinc(II) were subjected to an NMR study.[113] It was found that the chemical shift of the amino protons showed a correlation with σ^*, electron withdrawing groups causing a considerable downfield shift relative to TMS. This would be expected on the basis of the IR results. It was noted that on coordination the NMR signals due to the amino protons were shifted downfield.

It has been found that adduct formation between primary aliphatic amines, substituted anilines and substituted pyridines and nickel(II), cobalt(II) and zinc(II) acetylacetonates causes a considerable shift of νM-O to lower frequencies, electron release by the adduct causing even further lowering of νM-O, presumably causing strengthening of the M-N bond. A study of the heats of reaction between $Cu(ACA)_2$ and a series of variously

7. COPPER(II) β-KETOIMINE COMPLEXES

It was intended that the investigation of the effect of substituents on a molecule would be extended to include a series of metal β-ketoimine (see section (1) of Discussion) complexes. With divalent metal ions, β-ketoimines form complexes of the type



analogous to the acetylacetonates described previously. Many compounds of this nature have been synthesized,[155] also similar compounds derived from HBZA and HDBM. The IR spectra of these compounds are similar to those of the related acetylacetonates.

On the basis of a report[156] in which three copper(II) complexes of β-ketoimines (R = H, CH_3, C_6H_5) had been synthesized, the preparation of a series of copper(II) complexes of the variously substituted β-ketoimines was investigated.

The complex where R = C_6H_5 formed with ease giving the expected C, H and N analysis results. Of the other two complexes described by HOLTZCLAW *et.al.*[156] the one where R = H could easily be prepared but the complex where R = CH_3 reverted to the complex where R = H. It was also found that use of any of the other β-ketoimines derived from primary aliphatic amines always yielded an identical product (R = H). This was substantiated by elemental microanalysis and by the IR spectra which were identical for all compounds. The R = CH_3 complex had been purified, according to the report, by sublimation and the R = H complex

by recrystallization from ethanol. The sublimation product of the R = H complex was found to have a different IR spectrum (identical to that reported for R = CH_3) but microanalysis indicated the same C, H and N content as the unsublimed material. It would therefore appear that the complex is changed in some way on sublimation.

The IR spectra of both the sublimed and the unsublimed complexes display two strong N-H stretches in the region 3200-3400 cm^{-1}, indicating that R = H in both cases. Clearly, therefore, the methyl complex described by HOLTZCLAW and colleagues[156] is in fact the R = H complex. Further evidence for this can be obtained from a paper concerning gas chromatographic studies on these complexes.[157] The supposed methyl complex is reported as giving an identical chromatogram to that obtained for the analogous R = H complex, the retention times of the two supposedly different complexes being identical.

Since β-ketoimine complexes are capable of existing in *cis* and *trans* forms, it was considered that sublimation may lead to a separation of these isomers. However, an X-ray crystallographic study[158] on the R = H complex indicates that it exists solely as the *trans* form. It is suggested here that the change on sublimation must arise either because the complex undergoes a certain amount of decomposition, or undergoes transformation of *trans* isomer into *cis*.

8. AN NMR STUDY OF SUBSTITUTED PYRIDINES

Since much of the work in this thesis is directly concerned with coordinated substituted pyridines, and since so little work has been published on the NMR spectra of free pyridines with specific reference to substituent effects, an NMR study of the substituted pyridines employed in previous sections was instigated.

From the theory of chemical shifts, substituent induced ring proton shifts should depend primarily on the π-electron charge density of the carbon atom to which the proton is bound, assuming substituent independence of the ring current effect and minimal long range substituent mass effects for *meta* and *para* protons. Although large variations in α-proton shielding accompanying β-substitution of ethylene are (qualitatively) those expected from the resonance effects of the substituents,[159] attempts to establish the relative importance of resonance and field effects on ring proton shifts in substituted aromatic and heterocyclic systems have led to some confusion. In one report[18] a linear correlation between $\Delta\delta p$ (the change in chemical shift, relative to benzene, of the proton *para* to the substituent) and the HAMMETT substituent parameter, σ_p, was interpreted as evidence that mesomeric effects largely govern the proton shieldings in monosubstituted benzenes. In another report[19] inductive effects were considered more important. The purpose of this investigation is to show that the confusion arises from the former absence of reliable parameters which measure these effects separately and to make use of the *F* and *R* values of SWAIN and LUPTON[117] to establish the relative importance of the resonance effect.

In this study the NMR spectra of forty-two variously substituted pyridines have been determined. This study encompasses only 2-, 3- and 4-substituted pyridines and any combination of two or three of these positions. The effect of the substituent can then be observed on the proton in the 6-position by employing the HAMMETT parameters σ_m or σ_p, depending upon the position of substitution. Substituents in the 5-position impart a steric effect upon the proton in the 6-position and hence cannot be considered in a study of this nature. Assignment of the proton signals in the NMR spectra of the substituted pyridines is based mainly on the work of BRUGEL.[23]

It is evident from Fig. 37 that the chemical shift of the proton in the 6-position is substituent sensitive, electron withdrawal by the substituent causing deshielding of the proton. The three major deviates are the halogenated pyridines. It would appear from the graph that electron releasing substituents have a greater effect upon the chemical shift than do electron withdrawing substituents. A similar result has been demonstrated[21] by an NMR study of 2-substituted pyridines. It was found that a correlation existed between the σ_p value of the 2-substituent and the chemical shift of the proton *para* to the substituent. Since the HAMMETT σ_m and σ_p values comprise both field and resonance effects, it is clearly impossible at this stage to determine which is more important in these compounds, the inductive effect or the mesomeric effect. The recent separation of HAMMETT parameters into their field and resonance components[117] establishes that σ_p comprises approximately equal contributions from F (47%) and R (53%), while σ_m

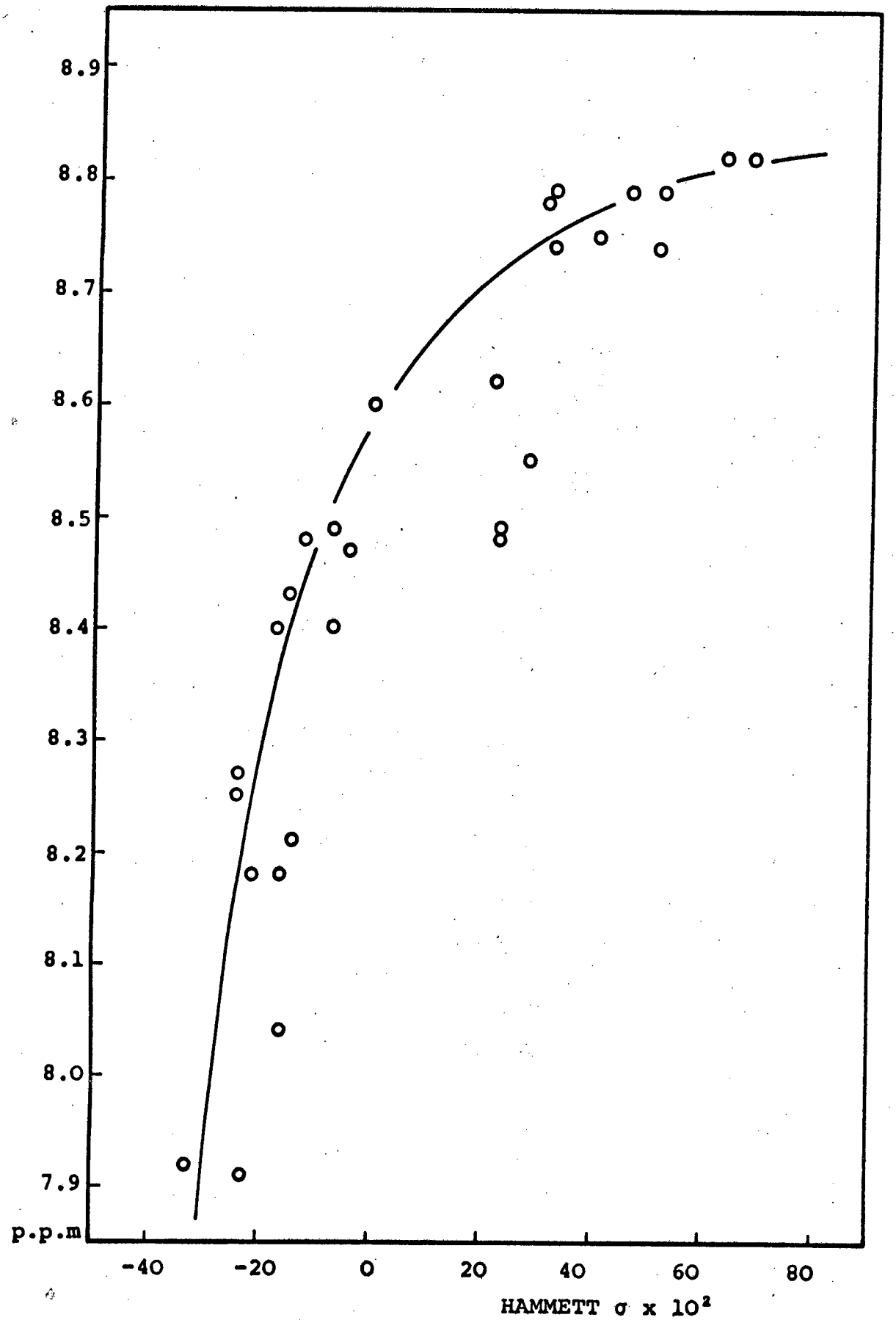


Fig. 37.

Relationship between σ and the chemical shift of the 6-proton in 2-, 3- and 4- substituted pyridines.

(78% F, 22% R) cannot be assumed free from a resonance contribution. Clearly the composition of σ_m and σ_p must largely invalidate earlier conclusions (made on the basis of the nature of $\Delta\delta/\sigma$ correlations) as to the relative importance of field and resonance effects.

Correlations between $\Delta\delta m$ and the parameters σ_m, F and R (Fig. 38) demonstrate the superiority of the pure resonance parameter R. Similar conclusions obtain for $\Delta\delta m$ in 3- and 4-substituted pyridines and monosubstituted benzenes. Correlations between $\Delta\delta p$ and the same parameters once again demonstrate the superiority of the resonance parameter R. Similar conclusions obtain for $\Delta\delta p$ in 2- and 3-substituted pyridines and monosubstituted benzenes. From the very obvious general scatter of points on the plots of $\Delta\delta$ against the field parameter F it would appear that field effects are of little importance in measurements of this nature. Reference to Table 3 shows that poor correlations between $\Delta\delta$ and σ stem largely from the anomalous shifts of the proton resonances in halogenated molecules in relation to the σ values, whereas the shifts are roughly those expected from the order of R values. The halogens exhibit maximum divergence of direction (sign) and magnitude of field and resonance components.

TABLE 3.

Proton chemical shifts ($\Delta\delta \times 10^2$; p.p.m.) of substituted benzenes and pyridines.

R	*Meta* protons				σ_m	R	F	σ_p	*Para* protons			
	Benzenes[a]		Pyridines[b]		$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$	Benzenes[a]		Pyridines[c]	
CN	-30		-21	-21	+68	+18	+85	+63	-30		-22	-36
$COCH_3$	-27		-17		+31	+20	+53	+52	-27		-19	-16
$CO_2C_2H_5$			-15	-13	+40	+14	+55	+52			-14	
C_6H_5			- 2		+22	- 9	+14	+ 1				
H	0	0	0	0	0	0	0	0	0	0	0	0
Cl	0	+ 2		+ 1	+37	-16	+69	+23	0	+12	+11	+ 6
Br	0	+ 8		+ 9	+39	-18	+73	+23	0	+ 3	+12	- 4
I	+17	+25		+15	+35	-20	+67	+28	+10	+ 3	+ 5	
F					+34	-34	+71	+ 6		+22		+17
$t\text{-}C_4H_9$			+12		-10	-14	-10	-20				
C_2H_5	+ 7		+13	+ 4	- 4	-11	- 6	-15	+ 7		+17	+20
CH_3	+10		+20	+ 7	- 7	-14	- 5	-17	+10		+20	+22
OH					0	-64	+49	-36	+37		+53	
NH_2	+13	+20	+42	+28	-16	-68	+ 4	-66	+40	+63	+69	+62

[a] First column: ref. 19, in cyclohexane;
Second column: ref. 18, in cyclohexane.

[b] First column: 4-substituted pyridines in deuterochloroform (this work);
Second column: 3-substituted pyridines in deuterochloroform (this work).

[c] First column: 3-substituted pyridines in deuterochloroform (this work);
Second column: 2-substituted pyridines in cyclohexane, ref. 21.

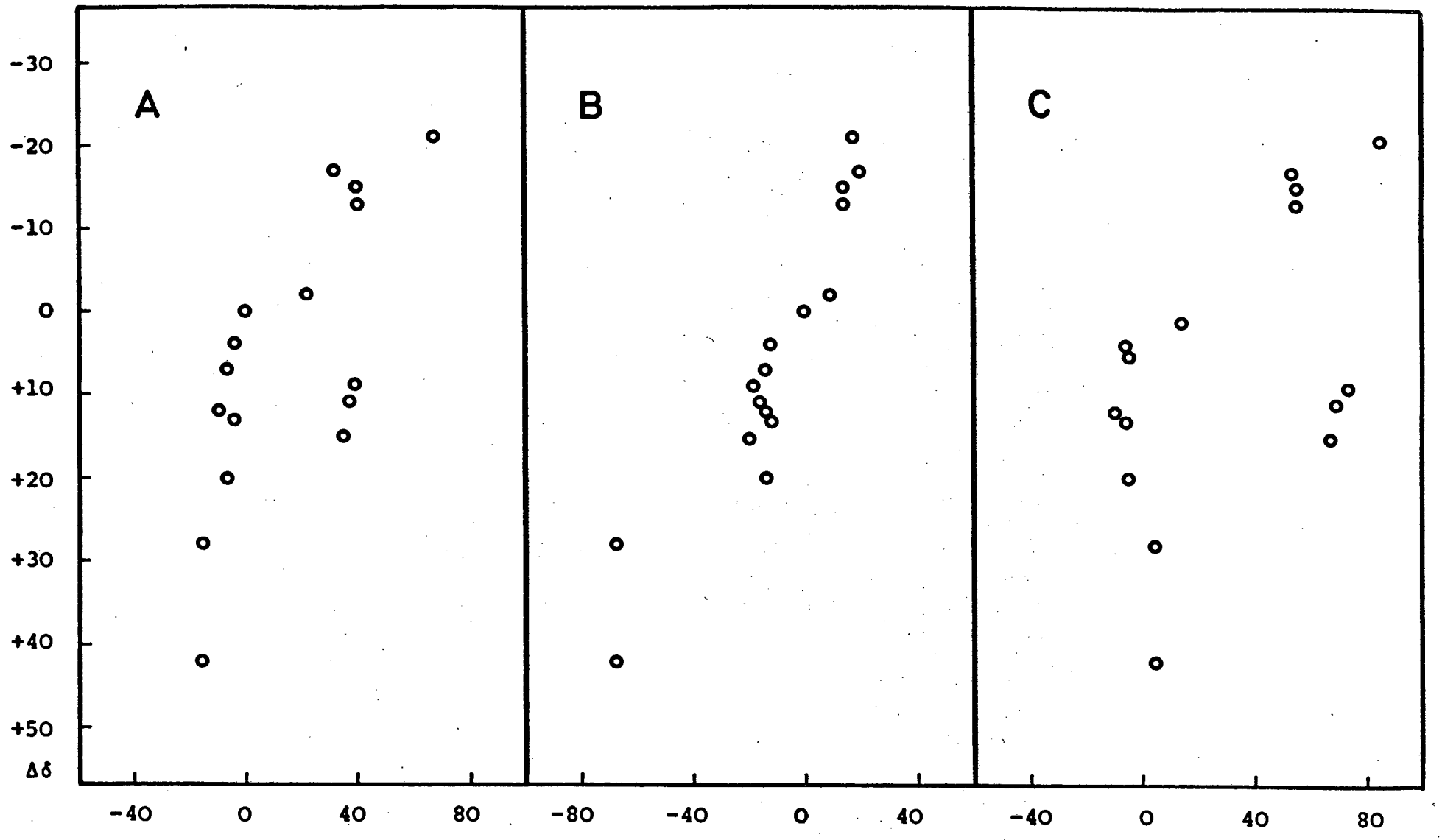


Fig. 38.

Relationship between chemical shifts ($\Delta\delta \times 10^2$ p.p.m.) and A; $\sigma_m \times 10^2$, B; $R \times 10^2$, C; $F \times 10^2$ for the *meta* protons of 3- and 4-substituted pyridines.

TABLE 4.

Proton chemical shifts ($\Delta\delta \times 10^2$; p.p.m.) for halogen substituted benzenes and pyridines.

R	*Meta* protons		*Para* protons		
	Benzenes[a]	Pyridines[b]	Benzenes[a]	Pyridines[c]	
F	+ 2·3	-	+22·0	-	+17
Cl	+ 2·5	+ 1	+12·0	+11	+ 6
Br	+ 8·0	+ 9	+ 3·0	+12	+ 4
I	+25·0	+15	+ 3·0	+ 5	-

[a]Ref. 18, in cyclohexane.

[b]3-substituted pyridines in deuterochloroform (this work).

[c]First Column: 3-substituted pyridines in deuterochloroform (this work).
Second Column: 2-substituted pyridines in cyclohexane, ref.21.

F is a pure non-resonance parameter in which the (spatial) field effect and the inductive effect on the σ-electrons (Iσ) are lumped together. R represents the total *ortho-para* directing effect comprising the mesomeric effect (M) and the inductive effect on the π-electrons (Iπ). The -Iσ effect of the halogens would be expected to deshield the *meta* and *para* protons while their combined +(M + Iπ) effect would shield the *para* proton and deshield the *meta* proton. If (as Fig. 38 implies) the -Iσ effect on proton shielding is small, the halogen with maximum +(M + Iπ) effect (fluorine) should exhibit maximum *para* proton shielding and minimum *meta* proton shielding. The most precise available results for halogen substituents indicate that this is observed (Table 4). The order of mesomeric effects of the halogens F < Cl < Br < I, revealed by π - π* shifts

in the electronic spectra of halogen substituted aromatic systems is that expected from their ionization potentials.[160] The total *ortho-para* directing effects are in the reverse order, and this order is revealed by ground state properties. That the values of $\Delta\delta$ imply the latter order of resonance effects is therefore entirely consistent with the dependence of shielding on π-electron density distribution rather than energy changes.

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Fig. 12.

Infrared Spectrum of $UO_2(DBM)_2 \cdot s\text{-}C_4H_9NH_2$